Patent No.: 6,746,782

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RD-26,970-2

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patentee:	Ji-Cheng Zhao et al.
Patent No.:	6,746,782
Issued:	June 8, 2004
Title:	DIFFUSION BARRIER COATINGS, AND RELATED ARTICLES AND PROCESSES

09/681,821

Attention: Certificate of Correction Branch
Commissioner for Patents
Alexandria, VA 22313-1450

Certificate
SEP 14 2004
of Correction

COVER LETTER

SIR:

Enclosed are the following documents for the above-identified patent:

1. A request for Certificate of Correction under 37 CFR 1.322.
2. A PTO Form 1050 Certificate of Correction.
3. A copy of the patent application as originally filed with drawings omitted.
4. A copy of the issued patent.
5. A copy of Amendment filed December 01, 2002.
6. A copy of Amendment filed May 25, 2003.
7. A copy of Amendment filed November 23, 2003.

Schenectady, New York

Dated: 2 Sept 2004

Respectfully submitted,

Paul J. DiConza

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17 SEP 2004

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REQUEST FOR CERTIFICATE OF CORRECTION UNDER 37 CFR 1.322

Attention: Certificate of Correction Branch
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S I R:

In accordance with 35 U.S.C.§254 and 37 C.F.R.§1.322, Patentee respectfully requests that the United States Patent and Trademark Office issue a certificate of correction for mistakes in the above identified patent, incurred through the fault of the Office, which mistakes are clearly disclosed in the records of the Office.

The patent contains several errors explained in Form PTO 1050 enclosed.

A copy of the patent application as filed is also enclosed for your convenience.

Since the mistakes were made by the Office and not by the Patentee, and is of consequence, and is clearly disclosed in the records of the Office, Patentee requests that the Office issue a certificate of correction without any fees charged to the Patentee.

If there are any questions regarding this matter please contact me.

Respectfully submitted,

Paul J. DiConza

Schenectady, New York

Dated: 2 Sept 2004

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PRINTER'S TRIM LILNE

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 6,746,782

DATED : June 8, 2004

INVENTOR(S) : Zhao et al.

It is certified that an error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Claim 8, Column 8, Line 2:
1 atom % to about 35 atom % of at learnt one element should read
1 atom % to about 35 atom % of at least one element

Claim 11, Column 8, Line 1:
The barrier coating material of claim 10, titer comprising should read
The barrier coating material of claim 10, further comprising

Claim 13, Column 8, Line 13:
(iii) an oxidation-resistant coning over the diffusion barrier should read
(iii) an oxidation-resistant coating over the diffusion barrier

Claim 20, Column 9, Line 3:
costing, and the diffusion barrier layer of component (ii) should read
coating, and the diffusion barrier layer of component (ii)

Claim 32, Column 10, Line10:
present the sum off (a), (b), (c), and (d) is no should read
present the sum of (a), (b), (c), and (d) is no

Claim 32, Column 10, Line 14:
group consisting of aluminide materials, MCrAI(X) should read
group consisting of aluminide materials, MCrAl(X)

Claim 33, Column 10, Line 3:
(b) about 10 atom % to about 60 stein % tungsten. should read
(b) about 10 atom % to about 60 atom % tungsten.

Claim 51, Column 12, Line 3:
aluminide materials, MCrAI(X) materials, and nickel- should read
aluminide materials, MCrAl(X) materials, and nickel -

MAILING ADDRESS OF SENDER:

Patent No. 6,746,782

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GENERAL ELECTRIC COMPANY
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FORM PTO 1050 (REV. 3-82)

17 SEP 2004

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UNITED STATES PATENT AND TRADEMARK OFFICE

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FORM PTO 1050 (REV. 3-82)

17 SEP 2004

DIFFUSION BARRIER COATINGS, AND RELATED ARTICLES AND PROCESSES

BACKGROUND OF THE INVENTION

[0001] This invention generally relates to coating systems for protecting metal substrates. More specifically, the invention is directed to a diffusion barrier layer disposed between a superalloy substrate and a protective coating for the substrate.

[0002] Metal components are used in a wide variety of industrial applications, under a diverse set of operating conditions. As an example, the various superalloy components used in turbine engines are exposed to high temperatures, e.g., above about 750°C. Moreover, the alloys may be subjected to repeated temperature cycling, e.g., exposure to high temperatures, followed by cooling to room temperature, and then followed by rapid re-heating. These components thus require coatings which protect them against oxidation and corrosion attack.

[0002] Various types of coatings are used to protect superalloys and other types of high-performance metals. One type is based on a material like MCrAl(X), where M is nickel, cobalt, or iron, and X is an element as described below. The MCrAl(X) coatings can be applied by many techniques, such as high velocity oxy-fuel (HVOF); plasma spray, or electron beam-physical vapor deposition (EB-PVD). Another type of protective coating is an aluminide material, such as nickel-aluminide or platinum-nickel-aluminide. Many techniques can be used to apply these coatings. For example, platinum can be electroplated onto the substrate, followed by a diffusion step, which is then followed by an aluminiding step, such as pack aluminiding. These types of coatings usually have relatively high aluminum content as compared to the superalloy substrates. The coatings often function as the primary protective layer (e.g., an environmental coating). As an alternative, these coatings can serve as bond layers for subsequently-applied overlayers, e.g., thermal barrier coatings (TBC's).

[0004] When the protective coatings and substrates are exposed to a hot, oxidative, corrosive environment (as in the case of a gas turbine engine), various metallurgical processes occur. For example, a highly-adherent alumina (Al_2O_3) layer ("scale") usually forms on top of the protective coatings. This oxide scale is usually very desirable because of the protection it provides to the underlying coating and substrate.

[0005] At elevated temperatures, there is often a great deal of interdiffusion of elemental components between the coating and the substrate. The interdiffusion can change the chemical characteristics of each of these regions, while also changing the characteristics of the oxide scale. In general, there is a tendency for the aluminum from the aluminum-rich protective layer to migrate inwardly toward the substrate. At the same time, traditional alloying elements in the substrate (e.g., a superalloy), such as cobalt, tungsten, chromium, rhenium, tantalum, molybdenum, and titanium, tend to migrate from the substrate into the coating. (These effects occur as a result of composition gradients between the substrate and the coating).

[0006] Aluminum diffusion into the substrate reduces the concentration of aluminum in the outer regions of the protective coatings. This reduction in concentration will reduce the ability of the outer region to regenerate the highly-protective alumina layer. Moreover, the aluminum diffusion can result in the formation of a diffusion zone in an airfoil wall, which undesirably consumes a portion of the wall. Simultaneously, migration of the traditional alloying elements like molybdenum and tungsten from the substrate into the coating can also prevent the formation of an adequate protective alumina layer.

[0007] A diffusion barrier between the coating and the substrate alloy can prolong coating life by eliminating or greatly reducing the interdiffusion of elemental components, as discussed above. Diffusion barrier layers have been used for this purpose in the past, as exemplified by U.S. Patent 5,556,713, issued to Leverant. The Leverant patent describes a diffusion barrier layer formed of a submicron layer of rhenium (Re). While such a layer may be useful in some situations, there are

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considerable disadvantages as well. For example, as the temperature increases, e.g., the firing temperature for a turbine, interdiffusion between the coating and the substrate becomes more severe. The very thin layer of rhenium may be insufficient for reducing the interdiffusion. A thicker barrier layer of rhenium could be used, but there would be a substantial mismatch in CTE (coefficient of thermal expansion) between such a layer and a superalloy substrate. The CTE mismatch may cause the overlying coating to spall during thermal cycling of the part. Moreover, rhenium can be oxidized rapidly, which may also induce premature spallation of the coating.

[0008] It should thus be apparent that new barrier coatings which overcome some of the drawbacks of the prior art would be welcome for high-temperature metal substrates. First and foremost, the barrier coatings should have relatively low "interdiffusivity" for aluminum and substrate elements. The barrier coatings should also be chemically compatible with the substrate alloy and any protective coating for the substrate. They should also be chemically and compositionally stable - especially during anticipated service lives (e.g., for turbine airfoils) at temperatures of greater than about 750°C. Moreover, the barrier coatings should exhibit a relatively high level of adhesion to both the substrate and the protective coating. The barrier coatings should also exhibit only a minimal CTE mismatch with the substrate and coating. Furthermore, the barrier coating should be capable of deposition by conventional techniques, such as plasma spray, physical vapor deposition, sputtering, and the like.

SUMMARY OF THE INVENTION

[0009] The needs described above have been addressed by the discovery of a barrier coating material, comprising:

[0010] (a) about 15 atom % to about 95 atom % chromium; and

[0011] (b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

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[0012] The barrier coating material often includes other constituents as well. For example, it may include about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof. It can also include about 1 atom % to about 35 atom % aluminum. Many of the factors involved in the selection of the composition of the barrier coating material are described below.

[0013] Another embodiment of the invention is directed to an article for use in a high-temperature, oxidative environment. The article includes a metal-based substrate (e.g., a superalloy), containing aluminum and other alloy elements, and an oxidation-resistant coating. Exemplary oxidation-resistant coatings are described below, e.g., aluminide materials, MCrAl(X) materials, and nickel-chrome materials. A barrier coating is disposed between the substrate and the oxidation-resistant coating.

[0014] The barrier layer performs several important functions. When the overlying oxidation-resistant coating is aluminum-rich, the barrier layer prevents the substantial migration of aluminum from such a coating into the substrate. (As used herein, an "aluminum-rich" coating is defined as one having a concentration of aluminum higher than the concentration of aluminum in the substrate. When comparing comparative, cross-sectional areas of the coating and the substrate, the concentration of aluminum in the coating is often about two times to about five times the concentration of aluminum in the substrate, prior to any heat treatment.).

[0015] The barrier layer also prevents the substantial migration of various substrate elements into the coating. In this manner, the integrity and service life of the coating system and the underlying substrate (e.g., a turbine airfoil) is significantly enhanced. As used herein, the "prevention of substantial migration" of aluminum from an aluminum-rich coating into the substrate refers to the amount of migration which occurs during anticipated service lives for the component at temperatures of greater than about 750°C. (Service lives for turbine engine components for the purpose of this explanation range from about 1000 hours to about 30,000 hours). For the present invention, less than about 10% of the aluminum migrates from the coating

into the substrate, when a barrier layer is present. Very often, the amount of migration is less than about 5%. In general, the migration levels for various alloy elements (as described below) from the substrate into the aluminum-rich coating are also reduced to these levels, in the presence of the barrier layer.

[0016] Another embodiment of this invention relates to a method for preventing the substantial migration of aluminum from an aluminum-rich, oxidation-resistant coating into an underlying metal-based substrate, in a high-temperature, oxidative environment. The method includes the step of incorporating a diffusion barrier layer between the substrate and the coating. The composition of such a layer is mentioned above, and further described below. Methods for providing effective coating systems over superalloy substrates also constitute part of this invention. These methods include the deposition of the diffusion barrier layer, an overlying oxidation-resistant layer, and a ceramic overcoat, e.g., a TBC.

[0017] Further details regarding the various features of this invention are found in the remainder of the specification.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is a cross-sectional micrograph of a protective coating system applied over a superalloy substrate.

DETAILED DESCRIPTION OF THE INVENTION

[0019] As mentioned above, an embodiment of this invention is directed to a barrier coating material for a metal component, such as a turbine blade or vane. As used herein, "barrier coating" (or "barrier layer") is meant to describe a layer of material which prevents the substantial migration of aluminum from an overlying coating to an underlying substrate. In preferred embodiments, the barrier coating also prevents the substantial migration of alloy elements of the substrate into the coating. Non-limiting examples of alloy elements for the substrate are nickel, cobalt, iron, aluminum, chromium, refractory metals, hafnium, carbon, boron, yttrium, titanium,

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and combinations thereof. Of that group, those elements which often have the greatest tendency to migrate into the overlying coating at elevated surface temperatures are cobalt, molybdenum, titanium, tantalum, carbon, and boron. The barrier coatings are also relatively thermodynamically and kinetically stable at the service temperatures encountered by the metal component.

[0020] As mentioned above, the barrier coating material includes about 15 atom % to about 95 atom % chromium. The specific amount of chromium present will depend on various factors. These include: the particular composition of the substrate and any coating applied over the barrier coating; the intended end use for the article (e.g., a turbine part); the expected temperature and temperature patterns to which the article itself will be subjected; and the desired service life of the barrier coating. In some embodiments, relatively high amounts of chromium are preferred, e.g., about 50 atom % to about 95 atom %, based on total atomic percent (atom %) of the barrier coating material. Especially preferred compositions of this type include a chromium level in the range of about 65 atom % to about 95 atom %. In other embodiments, the level of chromium is lower, but is still substantial, e.g., about 25 atom % to about 60 atom %, and preferably, about 35 atom % to about 55 atom %.

[0021] The barrier coating material also comprises about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof. Selection of a particular element (or elements) in that group will also depend on many of the factors discussed above. In some embodiments, the preferred level of rhenium is usually in the range of about 15 atom % to about 35 atom %, and most preferably, in the range of about 20 atom % to about 30 atom %. In other embodiments, the preferred level of rhenium is in the range of about 40 atom % to about 60 atom %.

[0022] The preferred level of tungsten is usually in the range of about 5 atom % to about 20 atom %, and most preferably, in the range of about 10 atom % to about 15 atom %. The preferred level of ruthenium is usually in the range of about 10 atom

% to about 60 atom %, and most preferably, in the range of about 20 atom % to about 40 atom %.

[0023] Very often (but not always), the barrier coating material further comprises about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, and iron. Various combinations of these elements are also possible. Their presence is often preferred when the barrier coating is being applied over a superalloy substrate, which contains one or more of these elements. Preferred ranges for each of these elements are as follows: Nickel: about 5 atom % to about 30 atom %; cobalt: about 2 atom % to about 15 atom %; and iron: about 2 atom % to about 15 atom %. In many embodiments, the preferred barrier coating constituent of this group is nickel, or a combination of nickel and cobalt, e.g., a combination with a nickel/cobalt ratio (by atom percent) in the range of about 99 : 1 to about 50 : 50.

[0024] The barrier coating material may also include aluminum (with or without nickel, cobalt, or iron). The presence of aluminum is preferred for embodiments in which relatively high levels of aluminum are present in the substrate, and/or in a coating applied over the barrier coating. (In this context, "relatively high aluminum levels" refers to amounts greater than about 10 atom % for the substrate, and amounts greater than about 40 atom % for the coating over the barrier coating). When present, the level of aluminum in the barrier coating material is usually in the range of about 1 atom % to about 35 atom %. In preferred embodiments, the aluminum is present at a level in the range of about 1 atom % to about 15 atom %. In some especially preferred embodiments, the aluminum is present at a level in the range of about 1 atom % to about 10 atom %.

[0025] Table 1 lists some of the more specific compositions which fall within the scope of this invention, and are preferred in some embodiments. All quantities are in atom percent, and based on 100 atom % for the entire composition:

TABLE 1

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(I)	Aluminum-	about 1-5%	(II)	Aluminum	about 1-5%

	Tungsten-	about 5-20%		Rhenium	about 15-35%
	Base Metal*-	about 25-35%		Base Metal*-	about 5-15%
	Chromium-	balance**		Chromium	balance**
(III)	Aluminum-	about 1-5%	(IV)	Aluminum-	about 1-5%
	Ruthenium-	about 10-60%		Rhenium-	about 40-60%
	Base Metal*-	about 20-35%		Base Metal*-	about 1-20%
	Chromium-	balance**		Chromium-	balance**

[0026] *Base metal" as used herein refers to one or more of the superalloy metals: nickel, cobalt, or iron. The preferred base metal is often nickel, or a combination of nickel and cobalt.

[0027] ** Cr is always present at a level of at least about 15 atom %.

[0028] In some alternative embodiments, these alloy compositions may further include relatively minor amounts of other elements. For example, they may include at least one component selected from the group consisting of zirconium, titanium, hafnium, silicon, boron, carbon, tantalum, ruthenium, molybdenum, and yttrium. The total amount of these other elements is usually in the range of about 0.1 atom % to about 5 atom %, and preferably, in the range of about 0.4 atom % to about 2.5 atom %.

[0029] Methods for combining the various alloy constituents into a desired coating material are well-known in the art. As a non-limiting example, the elements can be combined by induction melting, followed by powder atomization. Melt-type techniques for this purpose are known in the art, e.g., U.S. Patent 4,200,459, which is incorporated herein by reference.

[0030] Another embodiment of this invention is directed to an article that can be successfully employed in a high-temperature, oxidative environment. The article includes a metal-based substrate. While the substrate may be formed from a variety of different metals or metal alloys, it is usually a heat-resistant alloy, e.g., superalloys which typically have a maximum operating temperature of about 1000-1150°C.

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[0031] The term "superalloy" is usually intended to embrace complex cobalt-, nickel-, or iron-based alloys which include one or more other elements, such as chromium, rhenium, aluminum, tungsten, molybdenum, and titanium. Superalloys are described in various references, e.g., U.S. Patents 5,399,313 and 4,116,723, both incorporated herein by reference. High temperature alloys are also generally described in Kirk-Othmer's *Encyclopedia of Chemical Technology*, 3rd Edition, Vol. 12, pp. 417-479 (1980), and Vol. 15, pp. 787-800 (1981). The actual configuration of the substrate may vary widely. For example, the substrate may be in the form of various turbine engine parts, such as combustor liners, combustor domes, shrouds, buckets, blades, nozzles, or vanes.

[0032] The diffusion barrier layer is disposed over the substrate. In general terms, the barrier layer is formed of an alloy composition comprising:

[0033] (A) about 15 atom % to about 95 atom % chromium; and

[0034] (B) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

[0035] As described previously, the barrier layer alloy composition often includes other elements. Examples include one or more of the superalloy metals (Ni, Co, Fe). The alloy composition may also contain aluminum, as well as minor amounts of various other elements set forth above.

[0036] Methods for applying the barrier coating material over the substrate are well-known in the art. They include, for example, electron beam physical vapor deposition (EB-PVD); electroplating, ion plasma deposition (IPD); low pressure plasma spray (LPPS); chemical vapor deposition (CVD), plasma spray (e.g., air plasma spray (APS)), high velocity oxy-fuel (HVOF), sputtering, and the like. Very often, single-stage processes can deposit the entire coating chemistry. Those skilled in the art can adapt the present invention to various types of equipment. For example,

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the alloy coating elements could be incorporated into a target in the case of ion plasma deposition.

[0037] The thickness of the barrier layer will depend on a variety of factors. Illustrative considerations include: the particular composition of the substrate and the layer (or layers) applied over the barrier layer; the intended end use for the article; the expected temperature and temperature patterns to which the article itself will be subjected; and the intended service life and repair intervals for the coating system. When used for a turbine engine application (e.g., an airfoil), the barrier layer usually has a thickness in the range of about 1 micron to about 50 microns, and most often, in the range of about 5 microns to about 20 microns. It should be noted, though, that these ranges may be varied considerably to suit the needs of a particular end use. Moreover, for other types of applications, the thickness of the barrier layer can be as high as about 100 microns.

[0038] Sometimes, a heat treatment is performed after the barrier layer is applied over the substrate. The purpose of the heat treatment is to improve adhesion and to enhance the chemical equilibration between the barrier layer and the substrate. The treatment is often carried out at a temperature in the range of about 950°C to about 1200°C, for up to about 10 hours.

[0039} Various types of protective coatings may be applied over the barrier layer, depending on the service requirements of the article. In most cases, the coatings are selected to provide the necessary amount of oxidation resistance for the article. The oxidation-resistant coating is often an aluminide coating or an overlay coating. Examples of the former are nickel-aluminide, noble metal-aluminide, and nickel-noble metal-aluminide. Various techniques can be used to apply these coatings. For example, a noble metal such as platinum can first be electroplated onto the barrier layer. A diffusion step can then be carried out. The diffusion step can be followed by the deposition of a layer of nickel, cobalt, or iron (or any combination thereof). This Ni/Co/Fe layer can be applied over the surface by plating, spraying, or any other

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convenient means. An aluminiding step, such as pack aluminiding, can then be undertaken.

[0040] Alternatively, the Ni/Co/Fe layer can be applied first, followed by the deposition of the noble metal. The diffusion step can then be carried out, followed by the aluminiding step. Those of skill in the art can select the most appropriate coating technique and coating step-sequence for a given situation. Moreover, additional, conventional heat-treatment steps can be undertaken after the various deposition steps (including that of the TBC, mentioned below).

[0041] These types of coatings are often referred to as "diffusion coatings", and usually have relatively high aluminum content as compared to superalloy substrates. The coatings often function as the primary protective layer (e.g., an environmental coating). In the case of a turbine engine application, the aluminide coating usually has a thickness in the range of about 20 microns to about 200 microns, and most often, in the range of about 25 microns to about 75 microns.

[0042] Overlay coatings are known in the art, and generally have the composition MCrAl(X). In that formula, M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof. In contrast to diffusion coatings, overlay coatings are generally deposited intact, without reaction with any separately-deposited layers. Suitable techniques were mentioned above, e.g., HVOF, plasma spray, and the like. In the case of a turbine engine application, the overlay coating usually has a thickness in the range of about 20 microns to about 400 microns, and most often, in the range of about 35 microns to about 300 microns.

[0043] Another type of oxidation-resistant coating which may be used is a "chromia-former". Examples include nickel-chrome alloys, e.g., those containing from about 20 atom % to about 50 atom % chromium. Such coatings can be applied

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by conventional techniques, and often contain various other constituents as well, e.g., manganese, silicon, and/or rare earth elements.

[0044] In some embodiments of this invention, a ceramic coating, such as a TBC, can be applied over the oxidation-resistant coating. TBC's provide a higher level of heat resistance when the article is to be exposed to very high temperatures. TBC's are often used as overcoats for turbine blades and vanes. The TBC is usually (but not always) zirconia-based. As used herein, "zirconia-based" embraces ceramic materials which contain at least about 70% zirconia, by weight. In preferred embodiments, the zirconia is chemically stabilized by being blended with a material such as yttrium oxide (yttria), calcium oxide, magnesium oxide, cerium oxide, scandium oxide, or mixtures of any of those materials.

[0045] The thickness of the TBC will depend on many of the factors set forth above. Usually, its thickness will be in the range of about 75 microns to about 1300 microns. In preferred embodiments for end uses such as turbine engine airfoil components, the thickness is often in the range of about 75 microns to about 300 microns.

[0046] The micrograph of FIG. 1 is a general depiction of a coating system 10, suitable for deposition over metal-based substrate 12 (often a superalloy). A diffusion barrier layer 14 has been applied over layer 12, and a bond coat 16 is disposed over the diffusion barrier layer. A thermal barrier coating 18 is disposed over the bond coat.

[0047] Another embodiment of this invention is directed to a method for preventing the substantial migration of aluminum from an aluminum-rich, oxidation-resistant coating into an underlying superalloy substrate, in a high-temperature, oxidative environment. As described previously, aluminum diffusion into a substrate such as a turbine component can be a significant problem, e.g., in preventing the formation of a protective alumina layer.

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[0048] The method includes the step of disposing a diffusion barrier layer between the substrate and the oxidation-resistant coating, wherein the diffusion barrier layer comprises:

[0049] (a) about 15 atom % to about 95 atom % chromium; and

[0050] (b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

[0051] As described previously, the material which forms the barrier layer often includes other elements, such as aluminum and one or more of the superalloy metals (Ni, Co, Fe). As also mentioned above, a variety of techniques can be used to apply the diffusion barrier layer.

[0052] Specific embodiments of the present invention have been described. However, those skilled in the art will recognize that the present invention is capable of variations and modifications which fall within its scope. Thus, the embodiments presented herein are intended as typical of, rather than in any way limiting on, the scope of the invention as presented in the appended claims.

CLAIMS

What is claimed:

1. A barrier coating material, comprising:

(a) about 15 atom % to about 95 atom % chromium; and

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

2. The barrier coating material of claim 1, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

3. The barrier coating material of claim 1, further comprising about 1 atom % to about 35 atom % aluminum.

4. The barrier coating material of claim 1, wherein the level of chromium is in the range of about 25 atom % to about 60 atom %.

5. The barrier coating material of claim 1, wherein the level of tungsten is in the range of about 5 atom % to about 20 atom %.

6. The barrier coating material of claim 5, wherein the level of tungsten is in the range of about 10 atom % to about 15 atom %.

7. The barrier coating of claim 5, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

8. The barrier coating material of claim 5, further comprising about 5 atom % to about 30 atom % of nickel.

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9. The barrier coating material of claim 5, further comprising about 1 atom % to about 35 atom % aluminum.

10. The barrier coating material of claim 1, wherein the level of rhenium is in the range of about 15 atom % to about 35 atom %.

11. The barrier coating of claim 10, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

12. The barrier coating material of claim 10, further comprising about 1 atom % to about 35 atom % aluminum.

13. The barrier coating material of claim 1, wherein the level of ruthenium is in the range of about 10 atom % to about 60 atom %.

14. The barrier coating material of claim 13, wherein the level of ruthenium is in the range of about 20 atom % to about 40 atom %.

15. The barrier coating material of claim 13, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

16 The barrier coating material of claim 14, further comprising about 1 atom % to about 35 atom % aluminum.

17. The barrier coating material of claim 16, wherein the level of aluminum is in the range of about 1 atom % to about 15 atom %.

18. The barrier coating material of claim 1, wherein the level of rhenium is in the range of about 40 atom % to about 60 atom %.

19 The barrier coating material of claim 18, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

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20. The barrier coating material of claim 18, further comprising about 1 atom % to about 35 atom % aluminum.

21. An article for use in a high-temperature, oxidative environment, comprising:

(i) a metal-based substrate, comprising aluminum and other alloy elements;

(ii) a diffusion barrier layer overlying the substrate, said layer comprising

(A) about 15 atom % to about 95 atom % chromium; and

(B) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; and

(iii) an oxidation-resistant coating over the diffusion barrier layer.

22. The article of claim 21, wherein the level of chromium in the diffusion barrier layer is in the range of about 50 atom % to about 95 atom %.

23. The article of claim 21, wherein the level of chromium is in the range of about 25 atom % to about 60 atom %.

24. The article of claim 21, wherein the diffusion barrier layer further comprises about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

25. The article of claim 21, wherein the diffusion barrier layer further comprises about 1 atom % to about 35 atom % aluminum.

26. The article of claim 21, wherein the metal-based substrate is a superalloy, and comprises at least one base metal selected from the group consisting of nickel, cobalt, and iron.

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27. The article of claim 26, wherein the substrate further comprises at least one alloy element selected from the group consisting of cobalt, molybdenum, titanium, tantalum, carbon, and boron.

28. The article of claim 21, wherein the oxidation-resistant coating of component (iii) is an aluminum-rich coating, and the diffusion barrier layer of component (ii) prevents the substantial migration of aluminum from the aluminum-rich coating to the substrate, while also preventing the substantial migration of alloy elements of the substrate into the aluminum-rich coating.

29. The article of claim 28, wherein the aluminum-rich coating over the diffusion-barrier layer is an aluminide coating or an overlay coating.

30. The article of claim 29, wherein the aluminide coating is selected from the group consisting of nickel-aluminide; noble metal-aluminide, and nickel-noble metal-aluminide.

31. The article of claim 30, wherein the noble metal is platinum.

32. The article of claim 21, wherein the oxidation-resistant coating of component (iii) is an overlay coating having the composition MCrAl(X), where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof.

33. The article of claim 21, wherein the oxidation-resistant coating of component (iii) comprises a nickel-chrome alloy.

34. The article of claim 33, wherein the nickel-chrome alloy contains about 20 atom % to about 50 atom % chromium, and further comprises at least one element selected from the group consisting of manganese, silicon, and a rare earth element.

35. The article of claim 21, wherein the barrier layer has an average thickness in the range of about 1 micron to about 50 microns.

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36. The article of claim 35, wherein the barrier layer has an average thickness in the range of about 5 microns to about 20 microns.

37. The article of claim 21, further comprising a ceramic coating disposed over the oxidation-resistant coating of component (iii).

38. The article of claim 37, wherein the ceramic coating is a zirconia-based thermal barrier coating.

39. The article of claim 21, wherein the substrate is an airfoil of a gas turbine engine.

40. A turbine engine component for use in a high-temperature, oxidative environment, comprising:

(I) a superalloy substrate, comprising a nickel or nickel-cobalt alloy;

(II) a diffusion barrier layer overlying the substrate, said layer comprising

(a) about 15 atom % to about 95 atom % chromium;

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof;

(c) about 1 atom % to about 35 atom % of at least one element selected from at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(d) about 1 atom % to about 35 atom % aluminum;

(III) an oxidation-resistant coating over the diffusion barrier layer, comprising a material selected from the group consisting of aluminide materials, MCrAl(X) materials, and nickel-chrome materials,

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where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof; and

(IV) a zirconia-based thermal barrier coating over the oxidation-resistant coating.

41. A method for preventing the substantial migration of aluminum from an aluminum-rich, oxidation-resistant coating into an underlying metal-based substrate in a high-temperature, oxidative environment, comprising the step of disposing a diffusion barrier layer between the substrate and the coating, wherein the diffusion barrier layer comprises:

(a) about 15 atom % to about 95 atom % chromium; and

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

42. The method of claim 41, wherein the diffusion barrier layer is applied over the substrate by a technique selected from the group consisting of electron beam physical vapor deposition (EB-PVD); electroplating, ion plasma deposition (IPD); low pressure plasma spray (LPPS); chemical vapor deposition (CVD), plasma spray, high velocity oxy-fuel (HVOF), and sputtering.

43. The method of claim 41, wherein the metal based substrate comprises a superalloy.

44. The method of claim 41, wherein the oxidation-resistant coating is selected from the group consisting of aluminide materials, MCrAl(X) materials, and nickel-chrome materials, where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof.

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45. A method for providing a protective coating system over the surface of a superalloy substrate, comprising the following steps:

(i) applying a diffusion barrier layer overlying the substrate, said layer comprising

(A) about 15 atom % to about 95 atom % chromium; and

(B) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof;

(ii) applying an oxidation-resistant coating over the diffusion barrier layer; and then

(iii) applying a zirconia-based thermal barrier coating over the oxidation-resistant coating.

46. The method of claim 45, wherein the diffusion barrier layer further comprises:

(C) about 1 atom % to about 35 atom % of at least one element selected from at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(D) about 1 atom % to about 35 atom % aluminum.

47. The method of claim 45, wherein the superalloy substrate is an airfoil of a gas turbine engine.

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DIFFUSION BARRIER COATINGS, AND RELATED ARTICLES AND PROCESSES

ABSTRACT OF THE DISCLOSURE

[0052] A barrier coating is disclosed, containing about 15 atom % to about 95 atom % chromium; and about 5 atom % to about 60 atom % of at least one of rhenium, tungsten, and ruthenium. Nickel, cobalt, iron, and aluminum may also be present. The barrier coating can be disposed between a metal substrate (e.g., a superalloy) and an oxidation-resistant coating, preventing the substantial diffusion of various elements at elevated service temperatures. A ceramic overcoat (e.g., based on zirconia) can be applied over the oxidation-resistant coating. Related methods for applying protective coatings to metal substrates are also described.

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(54) **DIFFUSION BARRIER COATINGS, AND RELATED ARTICLES AND PROCESSES**

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(52) **U.S. Cl.** **428/632**; 428/655; 428/675; 428/678; 428/680; 428/656; 428/336; 420/428; 420/430; 420/432; 420/433; 420/437; 420/448; 420/37; 420/82; 420/588; 427/405; 427/455; 427/250; 427/531; 427/596; 204/192.15

(58) **Field of Search** 428/632, 655, 428/675, 678, 680, 672, 656, 336; 420/428, 430, 432, 433, 588, 462, 448, 37, 82, 113, 77, 114, 436, 437; 427/404, 405, 596, 531, 455, 250

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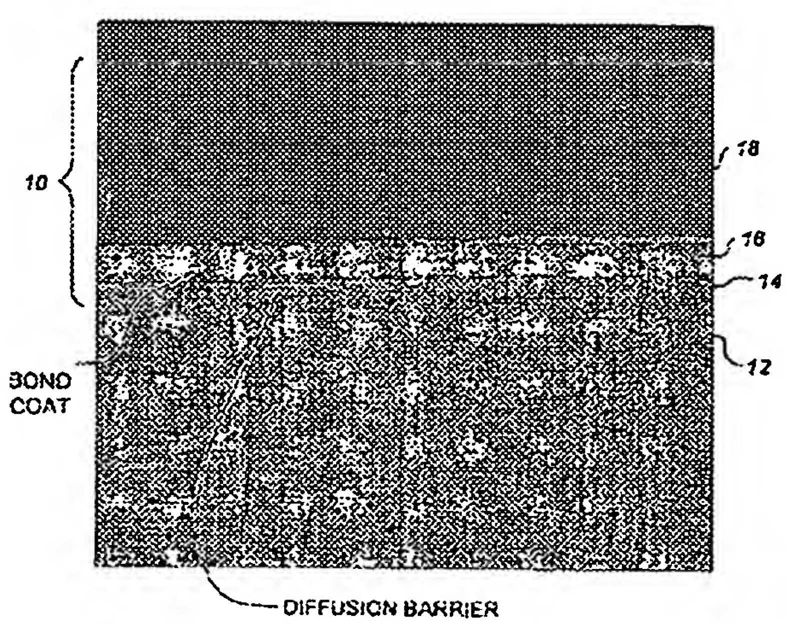
(57) **ABSTRACT**

A barrier coating is disclosed, containing about 15 atom % to about 95 atom % chromium; and about 5 atom % to about 60 atom % of at least one of rhenium, tungsten, and ruthenium. Nickel, cobalt, iron, and aluminum may also be present. The barrier coating can be disposed between a metal substrate (e.g., a superalloy) and an oxidation-resistant coating, preventing the substantial diffusion of various elements at elevated service temperatures. A ceramic overcoat (e.g., based on zirconia) can be applied over the oxidation-resistant coating. Related methods for applying protective coatings to metal substrates are also described.

54 Claims, 1 Drawing Sheet



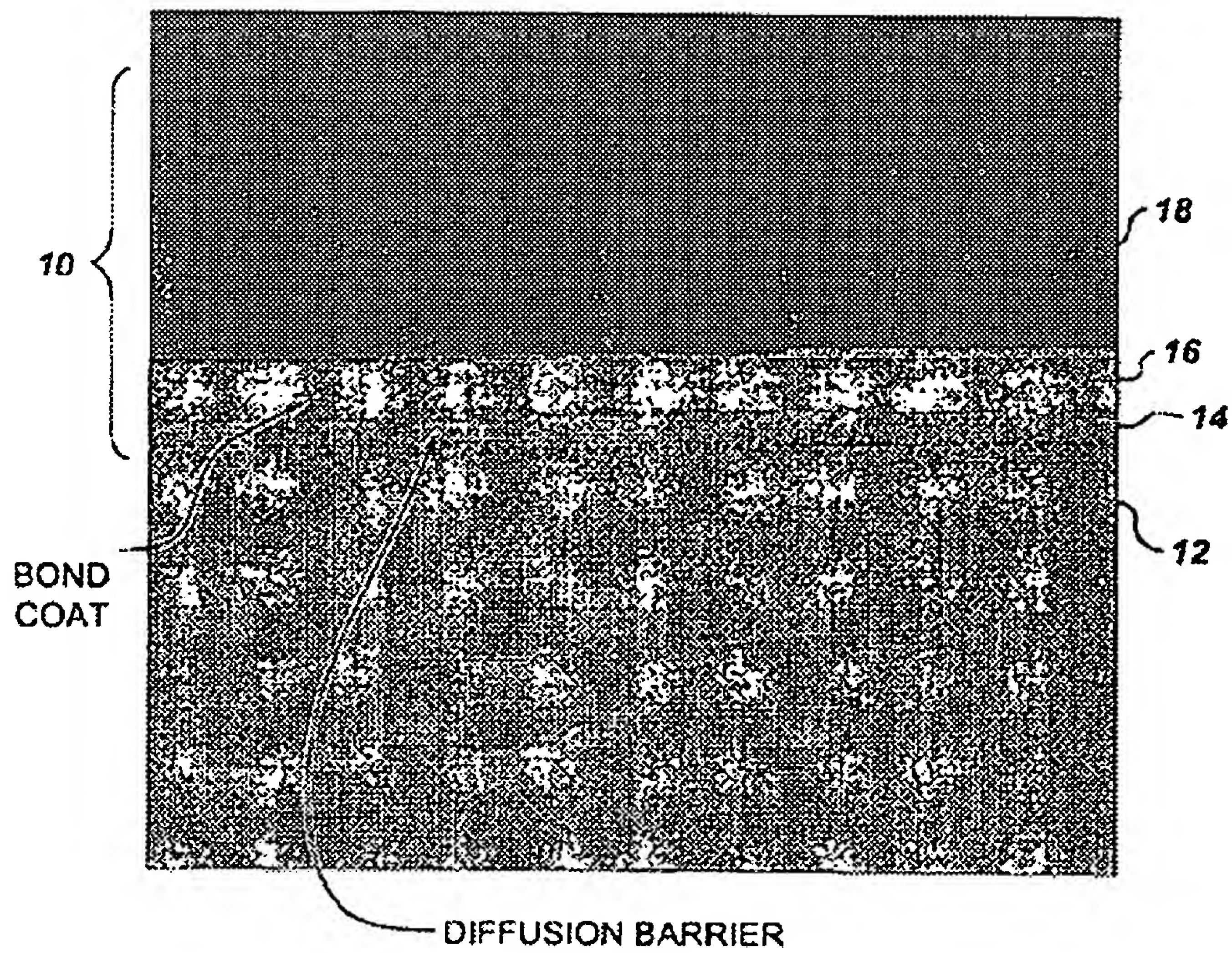


Fig. 1

DIFFUSION BARRIER COATINGS, AND RELATED ARTICLES AND PROCESSES

BACKGROUND OF INVENTION

This invention generally relates to coating systems for protecting metal substrates. More specifically, the invention is directed to a diffusion barrier layer disposed between a superalloy substrate and a protective coating for the substrate.

Metal components are used in a wide variety of industrial applications, under a diverse set of operating conditions. As an example, the various superalloy components used in turbine engines are exposed to high temperatures, e.g., above about 750C. Moreover, the alloys may be subjected to repeated temperature cycling, e.g., exposure to high temperatures, followed by cooling to room temperature, and then followed by rapid re-heating. These components thus require coatings which protect them against oxidation and corrosion attack.

Various types of coatings are used to protect superalloys and other types of high-performance metals. One type is based on a material like MCrAl(X), where M is nickel, cobalt, or iron, and X is an element as described below. The MCrAl(X) coatings can be applied by many techniques, such as high velocity oxy-fuel (HVOF); plasma spray, or electron beam-physical vapor deposition (EB-PVD). Another type of protective coating is an aluminide material, such as nickel-aluminide or platinum-nickel-aluminide. Many techniques can be used to apply these coatings. For example, platinum can be electroplated onto the substrate, followed by a diffusion step, which is then followed by an aluminiding step, such as pack aluminiding. These types of coatings usually have relatively high aluminum content as compared to the superalloy substrates. The coatings often function as the primary protective layer (e.g., an environmental coating). As an alternative, these coatings can serve as bond layers for subsequently-applied overlayers, e.g., thermal barrier coatings (TBC's).

When the protective coatings and substrates are exposed to a hot, oxidative, corrosive environment (as in the case of a gas turbine engine), various metallurgical processes occur. For example, a highly-adherent alumina (Al2O3) layer ("scale") usually forms on top of the protective coatings. This oxide scale is usually very desirable because of the protection it provides to the underlying coating and substrate.

At elevated temperatures, there is often a great deal of interdiffusion of elemental components between the coating and the substrate. The interdiffusion can change the chemical characteristics of each of these regions, while also changing the characteristics of the oxide scale. In general, there is a tendency for the aluminum from the aluminum-rich protective layer to migrate inwardly toward the substrate. At the same time, traditional alloying elements in the substrate (e.g., a superalloy), such as cobalt, tungsten, chromium, rhenium, tantalum, molybdenum, and titanium, tend to migrate from the substrate into the coating. (These effects occur as a result of composition gradients between the substrate and the coating).

Aluminum diffusion into the substrate reduces the concentration of aluminum in the outer regions of the protective coatings. This reduction in concentration will reduce the ability of the outer region to regenerate the highly-protective alumina layer. Moreover, the aluminum diffusion can result in the formation of a diffusion zone in an airfoil wall, which undesirably consumes a portion of the wall. Simultaneously, migration of the traditional alloying elements like molybdenum and tungsten from the substrate into the coating can also prevent the formation of an adequate protective alumina layer.

A diffusion barrier between the coating and the substrate alloy can prolong coating life by eliminating or greatly reducing the interdiffusion of elemental components, as discussed above. Diffusion barrier layers have been used for this purpose in the past, as exemplified by U.S. Pat. No. 5,556,713, issued to Leverant. The Leverant patent describes a diffusion barrier layer formed of a submicron layer of rhenium (Re). While such a layer may be useful in some situations, there are considerable disadvantages as well. For example, as the temperature increases, e.g., the firing temperature for a turbine, interdiffusion between the coating and the substrate becomes more severe. The very thin layer of rhenium may be insufficient for reducing the interdiffusion. A thicker barrier layer of rhenium could be used, but there would be a substantial mismatch in CTE (coefficient of thermal expansion) between such a layer and a superalloy substrate. The CTE mismatch may cause the overlying coating to spall during thermal cycling of the part. Moreover, rhenium can be oxidized rapidly, which may also induce premature spallation of the coating.

It should thus be apparent that new barrier coatings which overcome some of the drawbacks of the prior art would be welcome for high-temperature metal substrates. First and foremost, the barrier coatings should have relatively low "interdiffusivity" for aluminum and substrate elements. The barrier coatings should also be chemically compatible with the substrate alloy and any protective coating for the substrate. They should also be chemically and compositionally stable—especially during anticipated service lives (e.g., for turbine airfoils) at temperatures of greater than about 750C. Moreover, the barrier coatings should exhibit a relatively high level of adhesion to both the substrate and the protective coating. The barrier coatings should also exhibit only a minimal CTE mismatch with the substrate and coating. Furthermore, the barrier coating should be capable of deposition by conventional techniques, such as plasma spray, physical vapor deposition, sputtering, and the like.

SUMMARY OF INVENTION

The needs described above have been addressed by the discovery of a barrier coating material, comprising:(a)about 15 atom % to about 95 atom % chromium; and(b)about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

The barrier coating material often includes other constituents as well. For example, it may include about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof. It can also include about 1 atom % to about 35 atom % aluminum. Many of the factors involved in the selection of the composition of the barrier coating material are described below.

Another embodiment of the invention is directed to an article for use in a high-temperature, oxidative environment. The article includes a metal-based substrate (e.g., a superalloy), containing aluminum and other alloy elements, and an oxidation-resistant coating. Exemplary oxidation-resistant coatings are described below, e.g., aluminide materials, MCrAl(X) materials, and nickel-chrome materials. A barrier coating is disposed between the substrate and the oxidation-resistant coating.

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The barrier layer performs several important functions. When the overlying oxidation-resistant coating is aluminum-rich, the barrier layer prevents the substantial migration of aluminum from such a coating into the substrate. (As used herein, an "aluminum-rich" coating is defined as one having a concentration of aluminum higher than the concentration of aluminum in the substrate. When comparing comparative, cross-sectional areas of the coating and the substrate, the concentration of aluminum in the coating is often about two times to about five times the concentration of aluminum in the substrate, prior to any heat treatment.).

The barrier layer also prevents the substantial migration of various substrate elements into the coating. In this manner, the integrity and service life of the coating system and the underlying substrate (e.g., a turbine airfoil) is significantly enhanced. As used herein, the "prevention of substantial migration" of aluminum from an aluminum-rich coating into the substrate refers to the amount of migration which occurs during anticipated service lives for the component at temperatures of greater than about 750C. (Service lives for turbine engine components for the purpose of this explanation range from about 1000 hours to about 30,000 hours). For the present invention, less than about 10% of the aluminum migrates from the coating into the substrate, when a barrier layer is present. Very often, the amount of migration is less than about 5%. In general, the migration levels for various alloy elements (as described below) from the substrate into the aluminum-rich coating are also reduced to these levels, in the presence of the barrier layer.

Another embodiment of this invention relates to a method for preventing the substantial migration of aluminum from an aluminum-rich, oxidation-resistant coating into an underlying metal-based substrate, in a high-temperature, oxidative environment. The method includes the step of incorporating a diffusion barrier layer between the substrate and the coating. The composition of such a layer is mentioned above, and further described below. Methods for providing effective coating systems over superalloy substrates also constitute part of this invention. These methods include the deposition of the diffusion barrier layer, an overlying oxidation-resistant layer, and a ceramic overcoat, e.g., a TBC.

Further details regarding the various features of this invention are found in the remainder of the specification.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a cross-sectional micrograph of a protective coating system applied over a superalloy substrate.

DETAILED DESCRIPTION

As mentioned above, an embodiment of this invention is directed to a barrier coating material for a metal component, such as a turbine blade or vane. As used herein, "barrier coating" (or "barrier layer") is meant to describe a layer of material which prevents the substantial migration of aluminum from an overlying coating to an underlying substrate. In preferred embodiments, the barrier coating also prevents the substantial migration of alloy elements of the substrate into the coating. Non-limiting examples of alloy elements for the substrate are nickel, cobalt, iron, aluminum, chromium, refractory metals, hafnium, carbon, boron, yttrium, titanium, and combinations thereof. Of that group, those elements which often have the greatest tendency to migrate into the overlying coating at elevated surface temperatures are cobalt, molybdenum, titanium, tantalum, carbon, and boron.

The barrier coatings are also relatively thermodynamically and kinetically stable at the service temperatures encountered by the metal component.

As mentioned above, the barrier coating material includes about 15 atom % to about 95 atom % chromium. The specific amount of chromium present will depend on various factors. These include: the particular composition of the substrate and any coating applied over the barrier coating; the intended end use for the article (e.g., a turbine part); the expected temperature and temperature patterns to which the article itself will be subjected; and the desired service life of the barrier coating. In some embodiments, relatively high amounts of chromium are preferred, e.g., about 50 atom % to about 95 atom %, based on total atomic percent (atom %) of the barrier coating material. Especially preferred compositions of this type include a chromium level in the range of about 65 atom % to about 95 atom %. In other embodiments, the level of chromium is lower, but is still substantial, e.g., about 25 atom % to about 60 atom %, and preferably, about 35 atom % to about 55 atom %.

The barrier coating material also comprises about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof. Selection of a particular element (or elements) in that group will also depend on many of the factors discussed above. In some embodiments, the preferred level of rhenium is usually in the range of about 15 atom % to about 35 atom %, and most preferably, in the range of about 20 atom % to about 30 atom %. In other embodiments, the preferred level of rhenium is in the range of about 40 atom % to about 60 atom %.

The preferred level of tungsten is usually in the range of about 5 atom % to about 20 atom %, and most preferably, in the range of about 10 atom % to about 15 atom %. The preferred level of ruthenium is usually in the range of about 10 atom % to about 60 atom %, and most preferably, in the range of about 20 atom % to about 40 atom %.

Very often (but not always), the barrier coating material further comprises about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, and iron. Various combinations of these elements are also possible. Their presence is often preferred when the barrier coating is being applied over a superalloy substrate, which contains one or more of these elements. Preferred ranges for each of these elements are as follows: Nickel: about 5 atom % to about 30 atom %; cobalt about 2 atom % to about 15 atom %; and iron :about 2 atom % to about 15 atom %. In many embodiments, the preferred barrier coating constituent of this group is nickel, or a combination of nickel and cobalt, e.g., a combination with a nickel/cobalt ratio (by atom percent) in the range of about 99:1 to about 50:50.

The barrier coating material may also include aluminum (with or without nickel, cobalt, or iron). The presence of aluminum is preferred for embodiments in which relatively high levels of aluminum are present in the substrate, and/or in a coating applied over the barrier coating. (In this context, "relatively high aluminum levels" refers to amounts greater than about 10 atom % for the substrate, and amounts greater than about 40 atom % for the coating over the barrier coating). When present, the level of aluminum in the barrier coating material is usually in the range of about 1 atom % to about 35 atom %. In preferred embodiments, the aluminum is present at a level in the range of about 1 atom % to about 15 atom %. In some especially preferred embodiments, the aluminum is present at a level in the range of about 1 atom % to about 10 atom %.

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Table 1 lists some of the more specific compositions which fall within the scope of this invention, and are preferred in some embodiments. All quantities are in atom percent, and based on 100 atom % for the entire composition:

TABLE 1

(I)	Aluminum-	about 1–5%
	Tungsten-	about 5–20%
	Base Metal*-	about 25–35%
	Chromium-	balance**
(II)	Aluminum	about 1–5%
	Rhenium	about 15–35%
	Base Metal*-	about 5–15%
	Chromium	balance**
(III)	Aluminum-	about 1–5%
	Ruthenium-	about 10–60%
	Base Metal*-	about 20–35%
	Chromium-	balance**
(IV)	Aluminum-	about 1–5%
	Rhenium-	about 40–60%
	Base Metal*-	about 1–20%
	Chromium-	balance**

*"Base metal" as used herein refers to one or more of the superalloy metals: nickel, cobalt, or iron. The preferred base metal is often nickel, or a combination of nickel and cobalt.
**Cr is always present at a level of at least about 15 atom %.

In some alternative embodiments, these alloy compositions may further include relatively minor amounts of other elements. For example, they may include at least one component selected from the group consisting of zirconium, titanium, hafnium, silicon, boron, carbon, tantalum, ruthenium, molybdenum, and yttrium. The total amount of these other elements is usually in the range of about 0.1 atom % to about 5 atom %, and preferably, in the range of about 0.4 atom % to about 2.5 atom %.

Methods for combining the various alloy constituents into a desired coating material are well-known in the art. As a non-limiting example, the elements can be combined by induction melting, followed by powder atomization. Melt-type techniques for this purpose are known in the art, e.g., U.S. Pat. No. 4,200,459, which is incorporated herein by reference. Another embodiment of this invention is directed to an article that can be successfully employed in a high-temperature, oxidative environment. The article includes a metal-based substrate. While the substrate may be formed from a variety of different metals or metal alloys, it is usually a heat-resistant alloy, e.g., superalloys which typically have a maximum operating temperature of about 1000–1150C.

The term "superalloy" is usually intended to embrace complex cobalt-, nickel-, or iron-based alloys which include one or more other elements, such as chromium, rhenium, aluminum, tungsten, molybdenum, and titanium. Superalloys are described in various references, e.g., U.S. Pat. Nos. 5,399,313 and 4,116,723, both incorporated herein by reference. High temperature alloys are also generally described in Kirk-Othmer's *Encyclopedia of Chemical Technology,* 3rd Edition, Vol. 12, pp. 417–479 (1980), and Vol. 15, pp. 787–800 (1981). The actual configuration of the substrate may vary widely. For example, the substrate may be in the form of various turbine engine parts, such as combustor liners, combustor domes, shrouds, buckets, blades, nozzles, or vanes.

The diffusion barrier layer is disposed over the substrate. In general terms, the barrier layer is formed of an alloy composition comprising: (A) about 15 atom % to about 95 atom % chromium; and (B) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

As described previously, the barrier layer alloy composition often includes other elements. Examples include one or more of the superalloy metals (Ni, Co, Fe). The alloy composition may also contain aluminum, as well as minor amounts of various other elements set forth above.

Methods for applying the barrier coating material over the substrate are well-known in the art. They include, for example, electron beam physical vapor deposition (EB-PVD); electroplating, ion plasma deposition (IPD); low pressure plasma spray (LPPS); chemical vapor deposition (CVD), plasma spray (e.g., air plasma spray (APS)), high velocity oxy-fuel (HVOF), sputtering, and the like. Very often, single-stage processes can deposit the entire coating chemistry. Those skilled in the art can adapt the present invention to various types of equipment. For example, the alloy coating elements could be incorporated into a target in the case of ion plasma deposition.

The thickness of the barrier layer will depend on a variety of factors. Illustrative considerations include: the particular composition of the substrate and the layer (or layers) applied over the barrier layer; the intended end use for the article; the expected temperature and temperature patterns to which the article itself will be subjected; and the intended service life and repair intervals for the coating system. When used for a turbine engine application (e.g., an airfoil), the barrier layer usually has a thickness in the range of about 1 micron to about 50 microns, and most often, in the range of about 5 microns to about 20 microns. It should be noted, though, that these ranges may be varied considerably to suit the needs of a particular end use. Moreover, for other types of applications, the thickness of the barrier layer can be as high as about 100 microns.

Sometimes, a heat treatment is performed after the barrier layer is applied over the substrate. The purpose of the heat treatment is to improve adhesion and to enhance the chemical equilibration between the barrier layer and the substrate. The treatment is often carried out at a temperature in the range of about 950C to about 1200C, for up to about 10 hours.

Various types of protective coatings may be applied over the barrier layer, depending on the service requirements of the article. In most cases, the coatings are selected to provide the necessary amount of oxidation resistance for the article. The oxidation-resistant coating is often an aluminide coating or an overlay coating. Examples of the former are nickel-aluminide, noble metal-aluminide, and nickel-noble metal-aluminide. Various techniques can be used to apply these coatings. For example, a noble metal such as platinum can first be electroplated onto the barrier layer. A diffusion step can then be carried out. The diffusion step can be followed by the deposition of a layer of nickel, cobalt, or iron (or any combination thereof). This Ni/Co/Fe layer can be applied over the surface by plating, spraying, or any other convenient means. An aluminiding step, such as pack aluminiding, can then be undertaken.

Alternatively, the Ni/Co/Fe layer can be applied first, followed by the deposition of the noble metal. The diffusion step can then be carried out, followed by the aluminiding step. Those of skill in the art can select the most appropriate coating technique and coating step-sequence for a given situation. Moreover, additional, conventional heat-treatment steps can be undertaken after the various deposition steps (including that of the TBC, mentioned below).

These types of coatings are often referred to as "diffusion coatings", and usually have relatively high aluminum content as compared to superalloy substrates. The coatings often

function as the primary protective layer (e.g., an environmental coating). In the case of a turbine engine application, the aluminide coating usually has a thickness in the range of about 20 microns to about 200 microns, and most often, in the range of about 25 microns to about 75 microns.

Overlay coatings are known in the art, and generally have the composition MCrAl(X). In that formula, M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof. In contrast to diffusion coatings, overlay coatings are generally deposited intact, without reaction with any separately-deposited layers. Suitable techniques were mentioned above, e.g., HVOF, plasma spray, and the like. In the case of a turbine engine application, the overlay coating usually has a thickness in the range of about 20 microns to about 400 microns, and most often, in the range of about 35 microns to about 300 microns.

Another type of oxidation-resistant coating which may be used is a "chromia-former". Examples include nickel-chrome alloys, e.g., those containing from about 20 atom % to about 50 atom % chromium. Such coatings can be applied by conventional techniques, and often contain various other constituents as well, e.g., manganese, silicon, and/or rare earth elements.

In some embodiments of this invention, a ceramic coating, such as a TBC, can be applied over the oxidation-resistant coating. TBC's provide a higher level of heat resistance when the article is to be exposed to very high temperatures. TBC's are often used as overcoats for turbine blades and vanes. The TBC is usually (but not always) zirconia-based. As used herein, "zirconia-based" embraces ceramic materials which contain at least about 70% zirconia, by weight. In preferred embodiments, the zirconia is chemically stabilized by being blended with a material such as yttrium oxide (yttria), calcium oxide, magnesium oxide, cerium oxide, scandium oxide, or mixtures of any of those materials.

The thickness of the TBC will depend on many of the factors set forth above. Usually, its thickness will be in the range of about 75 microns to about 1300 microns. In preferred embodiments for end uses such as turbine engine airfoil components, the thickness is often in the range of about 75 microns to about 300 microns.

The micrograph of FIG. 1 is a general depiction of a coating system **10**, suitable for deposition over metal-based substrate **12** (often a superalloy). A diffusion barrier layer **14** has been applied over layer **12**, and a bond coat **16** is disposed over the diffusion barrier layer. A thermal barrier coating **18** is disposed over the bond coat.

Another embodiment of this invention is directed to a method for preventing the substantial migration of aluminum from an aluminum-rich, oxidation-resistant coating into an underlying superalloy substrate, in a high-temperature, oxidative environment. As described previously, aluminum diffusion into a substrate such as a turbine component can be a significant problem, e.g., in preventing the formation of a protective alumina layer.

The method includes the step of disposing a diffusion barrier layer between the substrate and the oxidation-resistant coating, wherein the diffusion barrier layer ccomprises: (a) about 15 atom % to about 95 atom % chromium; and (b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

As described previously, the material which forms the barrier layer often includes other elements, such as aluminum and one or more of the superalloy metals (Ni, Co, Fe). As also mentioned above, a variety of techniques can be used to apply the diffusion barrier layer.

Specific embodiments of the present invention have been described. However, those skilled in the art will recognize that the present invention is capable of variations and modifications which fall within its scope. Thus, the embodiments presented herein are intended as typical of, rather than in any way limiting on, the scope of the invention as presented in the appended claims.

What is claimed is:

1. A diffusion barrier coating, comprising:

(a) about 15 atom % to about 85 atom % chromium; and

(b) about 15 atom % to about 60 atom % rhenium.

2. The barrier coating material of claim **1**, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

3. The barrier coating material of claim **1**, further comprising about 1 atom % to about 35 atom % aluminum.

4. The barrier coating material of claim **3**, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

5. The barrier coating material of claim **3**, further comprising at least one element selected from the group consisting of tungsten, ruthenium, and mixtures of tungsten and ruthenium.

6. The barrier coating material of claim **1**, wherein the level of chromium is in the range of about 25 atom % to about 60 atom %.

7. The barrier coating material of claim **1**, wherein the level of rhenium is in the range of about 15 atom % to about 35 atom %.

8. The barrier coating of claim **7**, further comprising about 1 atom % to about 35 atom % of at learnt one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

9. The barrier coating material of claim **7**, further comprising about 1 atom % to about 35 atom % aluminum.

10. The barrier coating material of claim **1**, wherein the level of rhenium is in the range of about 40 atom % to about 60 atom %.

11. The barrier coating material of claim **10**, titer comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

12. The barrier coating material of claim **10**, further comprising about 1 atom % to about 35 atom % aluminum.

13. An article for use in a high-temperature, oxidative environment, comprising:

(i) a metal-based substrate, comprising aluminum and other alloy elements;

(ii) a diffusion barrier layer overlying the substrate, said layer comprising

(A) about 15 atom % to about 95 atom % chromium; and

(B) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; and

(iii) an oxidation-resistant coning over the diffusion barrier layer.

14. The article of claim **13**, wherein the level of chromium in the diffusion barrier layer is in the range of about 50 atom % to about 95 atom %.

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15. The article of claim 13, wherein the level of chromium is in the range of about 25 atom % to about 60 atom %.

16. The article of claim 13, wherein the diffusion barrier layer further comprises about 1 atom % to about 35 atom %, of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

17. The article of claim 13, wherein the diffusion barrier layer further comprises about 1 atom % to about 35 atom % aluminum.

18. The article of claim 13, wherein the metal-based substrate is a superalloy, and comprises at least one base metal selected from the group consisting of nickel, cobalt, and iron.

19. The article of claim 18, wherein the substrate further comprises at least one alloy element selected from the group consisting of aluminum, chromium, hafnium, yttrium, molybdenum, titanium, tantalum, carbon, and boron.

20. The article of claim 13, wherein the oxidation-resistant coating of component (iii) is an aluminum-rich costing, and the diffusion barrier layer of component (ii) prevents the substantial migration of aluminum from the aluminum-rich coating to the substrate, while also preventing the substantial migration of alloy elements of the substrate into the aluminum-rich coating.

21. The article of claim 20, wherein the aluminum-rich coating over the diffusion-barrier layer is an aluminide coating or an overlay coating.

22. The article of claim 21, wherein the aluminide coating is selected from the group consisting of nickel-aluminid; noble metal-aluminide, and nickel-noble metal-aluminide.

23. The article of claim 22, wherein the noble metal is platinum.

24. The article of claim 13, wherein the oxidation-resistant coating of component (iii) is an overlay coating having the composition MCrAl(X), where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof.

25. The article of claim 13, wherein the oxidation-resistant coating of component (iii) comprises a nickel-chromium alloy.

26. The article of claim 25, wherein the nickel-chromium alloy contains about 20 atom % to about 50 atom % chromium, and further comprises at least one element selected from the group consisting of manganese, silicon, mid a rare earth element.

27. The article of claim 13, wherein the barrier layer has an average thickness in the range of about 1 micron to about 50 microns.

28. The article of claim 27, wherein the barrier layer has an average thickness in the range of about 5 microns to about 20 microns.

29. The article of claim 13, further comprising a ceramic coating disposed over the oxidation-resistant coating of component (iii).

30. The article of claim 29, wherein the ceramic coating is a zirconia-based thermal barrier coating.

31. The article of claim 13, wherein the substrate is an airfoil of a gas turbine engine.

32. A turbine engine component for use in a high-temperature, oxidative environment, comprising:

(I) a superalloy substrate, comprising a nickel or nickel-cobalt alloy;

(II) a diffusion barrier layer overlying the substrate, said layer comprising

(a) about 15 atom % to about 95 atom % chromium;

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof;

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(d) about 1 atom % to about 35 atom % aluminum, wherein, for the maximum level of chromium present the sum off (a), (b), (c), and (d) is no greater than 100%;

(III) an oxidation-resistant coating over the diffusion barrier layer, comprising a material selected from the group consisting of aluminide materials, MCrAl(X) materials, and nickel-chromium materials,

where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof, and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof; and

(IV) a zirconia-based thermal barrier coating over the oxidation-resistant coating.

33. A diffusion barrier coating, comprising:

(a) about 15 atom % to about 90 atom % chromium; and

(b) about 10 atom % to about 60 stein % tungsten.

34. The diffusion barrier coating of claim 33, wherein the level of tungsten is in the range of about 10 atom % to about 20 atom %.

35. The diffusion barrier coating of claim 34, wherein the level of tungsten is in the range of about 10 atom % to about 15 atom %.

36. The barrier coating of claim 34, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

37. The barrier coating material of claim 34, further comprising about 5 atom % to about 30 atom % of nickel.

38. The barrier coating material of claim 34, further comprising about 1 atom % to about 35 atom % aluminum.

39. The barrier coating material of claim 38, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

40. The barrier coating material of claim 38, further comprising at least one element selected from the group consisting of rhenium, ruthenium, and mixtures of rhenium and ruthenium.

41. A barrier coating material, comprising:

(a) about 15 atom % to about 95 atom % chromium;

(b) about 10 atom % to about 60 atom % ruthenium; and

(c) about 1 atom % to about 15 atom % aluminum;

wherein, for the maximum level of chromium present the sum of (a), (b), and (c) is no greater than 100%.

42. The barrier coating material of claim 41, wherein the level of ruthenium is in the range of about 20 atom % to about 40 atom %.

43. The barrier coating material of claim 41, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

44. The barrier coating material of claim 41, further comprising at least one element selected from the group consisting of tungsten, rhenium, and mixtures of tungsten and rhenium.

45. A diffusion barrier coating having a thickness in the range of about 1 micron to about 50 microns, and consisting essentially of:

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(a) about 40 atom % to about 95 atom % chromium; and

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

46. A diffusion barrier coating, consisting essentially of

(a) about 15 atom % to about 95 atom % chromium;

(b) at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

the level of ruthenium is from about 5 atom % to about 60 atom %; and

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof,

wherein, for the maximum level of chromium present, the sum of(a), (b), and (c) is no greater than 100%.

47. A barrier coating material, consisting essentially of

(a) about 15 atom % to about 95 atom % chromium;

(b) at lest one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

the level of ruthenium is from about 5 atom % to about 60 atom %;

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(d) about 0.1 atom % to about 5 atom % of at least one element selected from the group consisting of zirconium, titanium, hafnium, silicon, boron, carbon, tantalum, molybdenum, and yttrium,

wherein, for the maximum level of chromium present, the sum of(a), (b), (c), and (d) is no greater than 100%.

48. A method for preventing the substantial migration of aluminum from an aluminum-rich, oxidation-resistant coating into an underlying metal-based substrate in a high-temperature, oxidative environment, comprising the step of disposing a diffusion barrier layer between the substrate and the coating, wherein the diffusion barrier layer comprises:

(a)about 15 atom % to about 95 atom % chromium; and

(b)about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

49. The method of claim 48, wherein the diffusion barrier layer Is applied over the substrate by a technique selected from the group consisting of electron beam physical vapor deposition (EB-PVD); electroplating, Ion plasma deposition (IPD); low pressure plasma spray (LPPS); chemical vapor deposition (CVD), plasma spray, high velocity oxy-fuel (HVOF), and sputtering.

50. The method of claim 48, wherein the metal based substrate comprises a superalloy.

51. The method of claim 48, wherein the oxidation-resistant coating is selected from the group consisting of aluminide materials, MCrAl(X) materials, and nickel-chrome materials, where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof.

52. A method for providing a protective coating system over the surface of a superalloy substrate, comprising the following steps:

(i)applying a diffusion barrier layer overlying the substrate, said layer comprising

(A) about 15 atom % to about 95 atom % chromium; and

(B) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof;

(ii)applying an oxidation-resistant coating over the diffusion barrier layer; and then (iii)applying a zirconia-based thermal barrier coating over the oxidation-resistant coating.

53. The method of claim 52, wherein the diffusion barrier layer further comprises:

(C) about 1 atom % to about 35 atom % of at least one element selected from at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(D) about 1 atom % to about 35 atom % aluminum.

54. The method of claim 52, wherein the superalloy substrate is an airfoil of a gas turbine engine.

* * * * *

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	
J. C. Zhao et al	:	Group Art Unit: 1775
Application No. 06/681,821	:	Examiner: J. McNeil
Filed: June 11, 2001	:	Response to Paper No. 4

For Diffusion Barrier Coatings, and
Related Articles and Processes

AMENDMENT

Honorable Assistant Commissioner for Patents,
Washington, DC 20231

Sir:

In response to the Office Action dated October 2, 2002, please enter the following amendment to the application, and consider the accompanying remarks.

IN THE CLAIMS:

Please cancel claims 41-47, without prejudice.

Please amend the claims, as follows:

1. (amended) A barrier coating material, comprising:

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(a) about 15 atom % to about 95 atom % chromium;

and

(b) about 15 atom % to about 60 atom % rhenium.

5. (amended) The barrier coating material of claim 48, wherein the level of tungsten is in the range of about 5 atom % to about 20 atom %.

13. (amended) The barrier coating material of claim 49, wherein the level of ruthenium is in the range of about 10 atom % to about 60 atom %.

Please add the following new claims:

New Claim 48. A barrier coating material, comprising:

(a) about 15 atom % to about 95 atom % chromium;

and

(b) about 5 atom % to about 60 atom % tungsten.

New Claim 49. A barrier coating material, comprising:

(a) about 15 atom % to about 95 atom % chromium;

(b) about 5 atom % to about 60 atom % ruthenium;

and

(c) about 1 atom % to about 15 atom % aluminum;

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

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New Claim 50. A barrier coating material, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

and

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

New Claim 51. A barrier coating material, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; and

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof,

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

New Claim 52. A barrier coating material, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

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(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof;

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(d) about 0.1 atom % to about 5 atom % of at least one element selected from the group consisting of zirconium, titanium, hafnium, silicon, boron, carbon, tantalum, ruthenium, molybdenum, and yttrium,

wherein, for the maximum level of chromium present, the sum of (a), (b), (c), and (d) is no greater than 100%.

REMARKS

Restriction Requirement

Claims 1-47 were originally submitted as part of the present application. They were made subject to a Restriction Requirement, resulting in two Groups: Claims 1-40 and claims 41-47. On August 6, 2002, a provisional election of group I (claims 1-40) was made by Applicant, with traverse. Applicant now affirms that election, and acknowledges the Examiner's reference to 37 CFR 1.142(b), regarding inventorship.

However, Applicant also continues to maintain that all of the originally-presented claims are part of one inventive concept, and can be examined as such. Claims 1-40 are directed to a product, i.e., a barrier coating material, as well as a multilayer article in which that material is incorporated.

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Claims 41-47 cover a method for preventing aluminum migration through regions of the article. The materials of claims 1-40, i.e., the barrier coating constituents, are identical to the barrier layer materials of claims 41-47. Moreover, the claimed process depends specifically on the presence of the claimed barrier material.

It is the Examiner' s view that the claimed product may be made by a materially different process. A casting process, using a mold, is provided as an example. However, Applicant submits that the illustration offered by the Examiner still includes the step of "disposing a diffusion barrier layer between the substrate and the coating". (Note, for example, that claim 41 is not restricted to any particular technique for applying the coating layers to the substrate.). Therefore, Applicant believes that the subject matter of Groups I and II is not distinct enough to warrant a Restriction Requirement.

Moreover, Applicant does not believe that Groups I and II have achieved "a separate status in the art", in a manner which mandates Restriction. The Examiner has recited different classes and subclasses for Groups I and II. However, the primary subject matter of all of the claims is the composition of the barrier layer. Applicant believes that such a common feature would result in relevant prior art being cross-referenced in both classification areas. In other words, "double searching" would not seem to be required, and the searching burden on the Examiner does not seem to be excessive. Applicant thus requests that the Restriction Requirement be withdrawn. In the interim, Applicant has canceled claims 41-47. The cancellation is being undertaken solely for the purpose of the fee calculation, and not to surrender any subject matter. The claims will be re-entered if the Examiner reconsiders the Restriction Requirement.

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Claim Rejections - 35 USC 102

The issue of anticipation under Section 102 can be reviewed more efficiently if the expression of the constituent-ranges for the compositions is standardized. The present inventors have expressed the composition of the clamed barrier layer in "atom percent", which is often a preferred type of unit for alloy "design" in this area. Conversion of the atom % values to weight percent can readily be carried out, using the atomic weights for each element. As an illustration for a given composition having constituents A, B, and C, in atom percent:

Weight % of A = (atom % of A) (atomic weight of A) / the sum (total) of :

[(atom % of A) (atomic weight of A) +
(atom % of B) (atomic weight of B) +
(atom % of C) (atomic weight of C)...]

The weight percent for components B and C (or however many components are present) can be calculated in the same manner. The value of the denominator in the illustrated equation (or for any composition being converted) will remain the same in each case. An example of a calculation for claim 1 (as originally filed) is as follows, using chromium with rhenium:

Atom %'s in Claim 1 (Assumption of Cr level of 40% if Re is 60%)

Cr	Re
95%	5%
40%	60%

Chromium atomic weight: 52.0
Rhenium atomic weight 186.2

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Conversion for higher level of Cr:

95(52) + 5(186.2) = (The "divisor")
4940 + 931 = 5871

Then, 4940/5871 x 100 = 84.1 <u>weight %</u> Cr
931/5871 x 100 = 15.9 <u>weight %</u>. Re

Conversion for lower level of Cr (and, thus, higher level of Re):

40(52) + 60(186.2) = (The "divisor")
2080 + 11,172 = 13,252

Then, 2080/13,252 x 100 = 15.7 <u>weight %</u> Cr
11,172/13,252 x 100 = 84.3 <u>weight %</u>. Re

All of the other conversions would follow the same procedure. A few of them are listed below, to facilitate discussion. In the case of claim 1, Applicant has provided the conversion for chromium with rhenium or with ruthenium. (The ranges for tungsten would be similar to those of rhenium, in view of the similarity in atomic weights).

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Chromium and Rhenium

Element	Atom Percent Range	Weight Percent Range
Chromium	40 - 95	15.7 - 84.1
Rhenium	5 - 60	15.9 - 84.3

Chromium and Ruthenium

Element	Atom Percent Range	Weight Percent Range
Chromium	40 - 95	25.5 - 90.7
Ruthenium	5 - 60	9.3 - 74.5

An exemplary conversion is offered for claim 2:

Chromium, Rhenium, and Nickel

Element	Atom Percent Range	Weight Percent Range
Chromium	15 - 94	5.8 - 83.2
Rhenium	5 - 60	15.8 - 83.3
Nickel	1 - 35	1.0 - 16.9

An exemplary conversion is offered for claim 3, as well:

Chromium, Rhenium, and Aluminum

Element	Atom Percent Range	Weight Percent Range
Chromium	15 - 94	6.2 - 83.6
Rhenium	5 - 60	15.9 - 84.4

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Aluminum	1 - 35	0.5 - 8.6

Applicant emphasizes that the choice of particular elements for the above conversions is merely exemplary, and not meant to indicate particular preferences, unless otherwise noted herein. The conversions should, however, facilitate the analysis under Section 102. (More conversions can be provided if the Examiner wishes).

Claims 1, 2, 5, 7, 10, 21, 23, 24-33, 37, 39 and 40 have been rejected under U.S.C. 102(b), as being anticipated by Chesnes, U.S. Patent 5,916,518. Chesnes is directed to braze alloy compositions. A number of specific compositions are described in the patent, e.g., see columns 5-7. As an example, the composition of col. 6, lines 35-48 includes, in weight % ("wt.%"): 10.5% Ni, 23% Cr, 1.5% Al, 1.75% Ti, 3% W, 1% Re, 6% Ta, 0-40 % Pt, 0-40% Pd, 0-0.55% C, 1.5% B, and 5% Si, with cobalt constituting the balance. The Examiner indicates (from cols. 5-6) that chromium can be present at a level of up to 40 wt.%; rhenium at a level of up to 15 wt.%; aluminum at a level of up to 12 wt.%; tungsten at a level of up to 15 wt.%; and nickel at a level of up to 10 wt.%.

A rejection of the claims under 35 U.S.C. 102(b) requires that each limitation of the claims be disclosed in the reference. In the present instance, Chesnes fails to contain all of the limitations present in Applicant's claim 1. With reference to the weight percentage ranges set forth above, Applicant notes that there is some overlap in the level of chromium. However, the level of rhenium and tungsten in Chesnes (i.e., component (b) of the claimed invention) is too low. The patent calls for a maximum of 15 wt.% for each element, while the <u>minimum</u> for rhenium and tungsten in pending claim 1 (as filed) is 15.9 wt.% and 15.7 wt.%, respectively. (The calculation for rhenium is provided above; tungsten's calculation is very similar). Moreover, the Chesnes reference fails to disclose the presence of the third possibility for

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component (b), i.e., ruthenium. Furthermore, the patent does not describe a "barrier coating material".

In regard to claim 2, there appears to be some overlap in regard to the nickel level in Chesnes. However, the limitations regarding Re, W, or Ru are still not met. The same holds true for the narrower ranges recited in claims 5 and 10. Chesnes also fails to anticipate claim 7. While there may be some overlap in regard to Ni/Co/Fe, the other limitation in the base claim (re Re/W/Ru) is still not met.

Chesnes also fails to describe the articles taught in claims 21, 23-33, 37, 39 and 40. As an example, the patent describes a metal-based substrate, but fails to describe a diffusion barrier layer - let alone one with the composition of claim 1. Moreover, while the reference describes various types of protective coatings for substrates, e.g., "MCrAl(X)" and ceramic coatings (col. 14, lines 57-65), it fails to disclose a coating structure which includes the barrier coating of the present invention. Thus, Applicant submits that Chesnes does not anticipate the claims at issue.

Claims 1-4 and 10-12 are rejected under U.S.C. 102(b), as being anticipated by Schmitz et al, U.S. Patent 5,993,980 ("Schmitz"). Schmitz describes a protective coating which includes a heat insulation layer. That layer includes the following primary components, expressed in weight %: 5-20% Re, 15-35% Cr, and 7-18% Al, with most of the balance consisting of cobalt and/or nickel (col. 3, lines 33-47). A variety of optional components can also be included, such as tungsten, at up to 12 wt.%.

In comparison to the present invention, Schmitz fails to disclose a barrier layer. Instead, Schmitz is describing a conventional "MCrAlY"-type coating which promotes adhesion between a substrate and a typical, ceramic top layer (See col. 3, lines 21-32).

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Rhenium is added to the coating of Schmitz, to enhance fatigue properties, as well as oxidation- and corrosion resistance (col. 4, lines 3-9). There appears to be a small amount of overlap between Schmitz and the present invention, in terms of chromium and the rhenium levels. However, Applicant has amended claim 1, so that the minimum level of rhenium for certain embodiments is now 15 atom %. This amount corresponds to about 38.7 wt.% - well above the maximum level of Schmitz. (The undersigned would be happy to provide the Examiner with the conversion-calculation, if requested. Other changes to claim 1 are discussed below.). Support for the new lower limit of rhenium can be found, for example, in paragraph 19 of the specification, third sentence. Applicant also wishes to emphasize that the modified language of claim 1, component (b), is still intended to cover the combination of rhenium with tungsten or ruthenium, or any combination thereof.

The level of tungsten (12 wt.%) in the Schmitz patent is lower than that required for the present invention. Moreover, Schmitz does not appear to disclose ruthenium. Furthermore, the differences noted above are also relevant to claims 10-12, which are primarily directed to more specific levels of rhenium. The lowest amount of Re present in Applicant's compositions will still be considerably greater than that of Schmitz, regardless of whether aluminum and Ni/Co/Fe components are also present (claims 11 and 13). Applicant thus submits that Schmitz does not anticipate the claims at issue.

Claims 1-12 stand rejected under U.S.C. 102(b), as being anticipated by Czech et al, U.S. Patent 5,582,635 ("Czech '635"). Chech '635 describes a protective coating consisting essentially of the following primary components, expressed in weight %: 25-40% Ni, 28-32% Cr, 7-9% Al, and

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0.5-2% silicon. Other optional components can be present as well, such as Re and W (both at 0-15 wt.%). (See col. 2, lines 9-29).

As in the two other references discussed above, Chech '635 fails to meet all of the limitations of the present invention. Again, there is some slight overlap in the amount of rhenium, but that overlap is eliminated by the amendment to claim 1. The level of tungsten (15% maximum) is below that of the present invention, as discussed previously in regard to the Chesnes patent. Moreover, Chech '635 fails to mention the presence of ruthenium for the coatings.

The differences noted above also serve to distinguish dependent claims 2-12 from Chech '635. Furthermore, the level of nickel in the patent is higher than that specified for claim 2 of the present invention (1.0 - 16.9 wt.% in Applicant's exemplified range, noted above). The same should be the case for alternative elements cobalt or iron in claim 2, which have atomic weights fairly close to that of nickel. Thus, Applicant submits that claims 1-12 are patentable over Chech '635.

Claims 1, 3, 4, 13, 14, 16 and 17 are rejected under U.S.C. 102(b), as being anticipated by Jackson, U.S. Patent 4,980,244. Jackson describes a composition consisting essentially of chromium, ruthenium, and aluminum. The components are present in proportions set forth within the bounds of curve A, as shown in the triaxial plot of FIG. 5 (see claim 1; col. 2, lines 60-64). A review of the plot appears to show the following approximate ranges for the components, in atom %**:** 32 at.% to 63 at.% chromium; 18 at.% to 35 at.% ruthenium; and 19 at.% to 35 at.% aluminum. As the Examiner can see, the tables in column 6 (as well as the tables in column 7) provide some conversions for exemplary compositions of Jackson.

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It is clear that Jackson fails to describe compositions which contain rhenium or tungsten. In fact, the compositions are generally restricted to the three components set forth above, although the patent alludes to compositions which may contain iron as well (e.g., Table III). Jackson also fails to describe the presence of a "barrier layer", as recited in the present claims. Moreover, the patent fails to describe Applicant's article, although the article claims do not appear to be at issue here.

However, Jackson does disclose compositions which overlap those of the present invention, in terms of ruthenium and aluminum content. In order to reduce issues in prosecution, Applicant has deleted ruthenium from claim 1, and recited the element in new claim 49. The new claim recites combinations of chromium and ruthenium in ranges previously set forth in claim 1. The claim further includes about 1 to 15 atom % aluminum. Such a range for aluminum is never disclosed in Jackson, which appears to have a minimum level of 19 atom %. Support for Applicant's range of aluminum is found, for example, in paragraph 22 of the specification, line 9. Thus Applicant submits that new claim 49 is patentable over Jackson.

The attention of the Examiner is briefly directed to the last phrase in claim 49, which indicates that the sum of the components must equal 100%. In other words, the phrase clarifies the fact that chromium cannot exceed 94 atom %, if ruthenium and aluminum are present at 5 atom % and 1 atom %, respectively. Applicant also notes that the claim, while distinguishing over Jackson, is still open-ended, allowing for the presence of other components. (The same type of phrasing has also been added to several of the new claims discussed below).

Claims 1-12 stand rejected under U.S.C. 102(b), as being anticipated by Czech et al, U.S. Patent 5,273,712 ("Czech '712"). The patent describes a protective coating for metal components. In general terms, the

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coating contains, in weight percent: 1-20% Re, 15-50% Cr, 0-15% Al, and most of the balance consisting of Fe, Ni, or Co (col. 1, line 59- col. 2, line 19). A variety of elective components can also be present, such as silicon, yttrium, tungsten (0-12%), and zirconium. Moreover, a restriction on the combined quantity of chromium and aluminum is also described.

Clearly, Chech '712 mentions a coating composition which includes chromium, rhenium, and optionally, tungsten. However, the level of tungsten is lower than that specified for the present invention. Moreover, the level of rhenium is also below that recited in amended claim 1. The level of nickel is generally higher than that of the present invention, although there may be a slight amount of overlap.

In regard to Applicant's claim 3, there is some overlap in the respective levels of aluminum. However, that claim, like others (as filed), also requires relatively high levels of rhenium, tungsten, or ruthenium. The Chech '712 patent discloses insufficient levels of tungsten for the present invention, and also fails to even mention the presence of ruthenium. Furthermore, Chech '712 does not disclose a composition in the form of a barrier layer, as in the present invention. Applicant thus requests that this anticipation-rejection be withdrawn.

Claims 1-7 stand rejected under U.S.C. 102(e), as being anticipated by Nazmy et al, U.S. Patent 6,245,447 ("Nazmy"). This patent describes an iron-aluminide coating being used as a bonding layer. The coating includes, by weight: 5-35% Al, 15-25% Cr, 0.5-10% Mo, W, Ta, and/or Nb; 0-0.3% Zr, 0-1% B, and 0-1% Y, with the remainder being iron (col. 1, lines 37-48).

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Applicant emphasizes that Nazmy is clearly outside the scope of the present invention, when the formulations are compared with common units, i.e., weight percent. The level of tungsten is too low for the present invention. Moreover, the patent fails to disclose the presence of ruthenium or rhenium, and has nothing to do with a barrier layer.

A brief comment relative to several of the dependent claims is also in order. While there is overlap in the level of aluminum, the compositions of Nazmy do not appear to contain nickel. Moreover, they generally require large amounts of iron (e.g., see the tables in columns 1-3), which appear to be above the maximum for the present invention. For these reasons, Nazmy clearly does not anticipate the present invention.

Claims 1, 10, 13-15, 18-22, 26-33, and 35-39 are rejected under U.S.C. 102(e), as being anticipated by Spitsberg et al, U.S. Patent 6,306,524 ("Spitsberg"). This patent describes a coating used over a superalloy substrate. The coating includes a diffusion barrier layer as an intermediate layer between the substrate and an overlying protective coating. (A ceramic-type thermal barrier coating may also be employed as the top layer). The protective coating has a high content of aluminum (col. 3, lines 30-32). The diffusion barrier layer has a low diffusion permeability for aluminum from the coating. It may also have a low diffusion permeability for refractory elements which would migrate from the substrate.

A variety of coating compositions are described in the patent. (Note that, in this instance, they are expressed in atom percent, as in Applicant's claims). Most of the compositions contain very low levels of chromium, e.g., 5 atom % or less (col. 6, Table 1). However, several of the compositions which happen to be listed in that table include higher chromium levels, i.e., see alloys DB 12, 22, and 26. Moreover, DB 22 contains 15 atom % ruthenium, while DB 26 contains 35 atom % rhenium, which both appear to

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be within the scope of the present invention. Spitsberg also describes articles which are similar to those of the present invention, in terms of substrates and overlying protective coatings.

However, Spitsberg does not disclose tungsten in a composition like that of the present invention, e.g., in the Table 1 compositions of the patent, containing higher levels of chromium. Moreover, Spitsberg fails to disclose nickel, cobalt, or iron in such a composition. Furthermore, Spitsberg contains no disclosure of aluminum in any of the "higher-chromium" compositions.

It should be apparent that there are certainly differences between the teachings of Spitsberg and the present invention. However, Applicant is willing to advance prosecution by swearing behind the reference, with the attached Declaration under Rule 131. The Declaration is presently unsigned, but an executed copy can be submitted shortly. The exhibits provide evidence of the claimed invention being reduced to practice before the filing date of Spitsberg, March 24, 1999. Applicant submits that the Declaration should remove the reference from consideration in this context.

Claims 21 and 23-40 have been rejected under 35 U.S.C. 103(a), as being unpatentable over Czech '635, in view of Spitsberg et al, U.S. 6,306,524. Although this is not structured as an "obviousness-type" double patenting rejection, Applicant questions the status of Spitsberg as a reference. The question relates to the Rule 131 Affidavit submitted herewith, and to the possibility that the reference can alternatively be removed by way of Rule 130. (The present application and Spitsberg are commonly owned, and the patent is not prior art under 35 U.S.C. 102(b)). The undersigned would appreciate discussing this issue with the Examiner. In the meantime, however, Applicant will also reply substantively to the Section 103 rejection.

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In brief, one embodiment of the present invention is directed to a barrier coating material based on chromium and at least one of rhenium, tungsten, or ruthenium. Other components are present when certain end uses are contemplated for the coating material. For example, the superalloy elements, nickel, cobalt, or iron, are sometimes included, as is aluminum.

Another important embodiment of the invention is directed to an article which includes the barrier layer, e.g., a turbine engine part. As described in paragraphs 12 and 13 of the specification, the barrier layer is important for several functions - especially under high temperature conditions. For example, it prevents the substantial migration of aluminum from an aluminum -rich overlayer into the substrate. In this manner, the detrimental effects of diminished aluminum in the protective overlayer (see paragraph 6) can be substantially avoided. The presence of significant amounts of rhenium/tungsten/ruthenium, in combination with chromium, is critical to the specific objective of this invention. These refractory-type materials slow down diffusion, by restricting the solubility of aluminum in a higher-melting structured system. The barrier layer itself can also minimize the undesirable migration of various substrate elements into the protective coating, as described in the application.

Both of the applied references under 35 U.S.C. 103 have been described previously. The Examiner notes that Chech '635 teaches a protective coating having the composition described above, which includes, inter alia, 28-32 wt.% chromium, and 0-15 wt.% rhenium or tungsten. The absence of an overlying coating ("topcoat") like nickel aluminide or "MCrAlY" is also noted, and the Examiner mentions their presence in Spitsberg. The Examiner then states that it would have been obvious to one of ordinary skill in the art to apply the topcoats of Spitsberg to the protective coatings of Czech '635.

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It is true that the overcoats of Spitsberg - MCrAlY, platinum aluminide, or nickel aluminide - are generally identical to those of the present invention. However, Applicant submits that the coating of Czech '635 exemplified in the rejection is different from that of the present invention. Some of the compositional differences have been described previously. Furthermore, of even greater significance here is the fact that Czech '635 is simply describing a typical MCrAlX coating, used to protect a superalloy substrate from corrosion (col. 2, lines 9-24). Czech '635 has nothing to do with barrier coatings - let alone those that are based on Cr and Re/W/Ru. The fact that rhenium and tungsten levels are allowed to be at 0% demonstrates that Czech '635 never contemplates the present invention, which requires these refractories to restrict the migration of aluminum. (Ruthenium is not mentioned in the patent)

Applicant has previously noted some of the differences between Spitsberg and that of the present invention. Moreover, Spitsberg is primarily directed to compositions with relatively low levels of chromium (see Table 1). In contrast, the present inventors recognized that higher chromium levels in combination with Re/W/Ru are sometimes highly advantageous. Of the 28 compositions listed in Spitsberg' table, only two fall within the scope of the present invention. Applicant thus submits that the combination of Spitsberg with Czech '635 does not suggest an article like that of pending claims 21 and 23-40.

A brief note on some of the new claims would be appropriate. Claim 48 is directed to a barrier coating material which comprises chromium and tungsten. The claim is meant to embrace the original range of tungsten, since claim 1 had been amended to recite a narrower, specific range for rhenium. No new matter has been added, and it is intended that the claim embrace all combinations of tungsten with chromium and other elements, as originally presented in this Application. For example, the scope of the claim

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would also include the possibility of having Ni/Co/Fe and/or Al present (e.g., see claims 2 and 3, respectively). Moreover, component (b) of the claim is intended to cover the combination of tungsten with rhenium or ruthenium, or any combination thereof. Claim 5 has also been amended to properly depend from claim 48.

Claims 50-52 have been added to recite specific compositions preferred for some embodiments of the invention. Each claim utilizes the transitional term "consisting essentially of". However, it is the intention of the inventors that these claims may also include other components which do not substantially alter the properties of the compositions. Claim 50 is directed to compositions of Cr and at least one of Re/W/Ru. Claim 51 covers the subject matter of claim 50, in combination with at least one of Ni/Co/Fe. Finally, claim 52 embraces the subject matter of claim 51, in combination with at least one of the elements of component (d). (Those elements are described in paragraph 26 of the specification, second sentence). No new matter has been added by way of these new claims, and Applicant submits that they are novel and nonobvious in view of the cited references.

In conclusion, Applicant submits that the amended claims are now in allowable form, as are the new claims. The undersigned suggests that any remaining issues can be resolved by a telephone conference.

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Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	
J. C. Zhao et al	:	Group Art Unit: 1775
Application No. 06/681,821	:	Examiner: J. McNeil
Filed: June 11, 2001	:	Response to Paper No. 7
For Diffusion Barrier Coatings, and Related Articles and Processes		

AMENDMENT

Honorable Assistant Commissioner for Patents,
Washington, DC 20231

Sir:

In response to the Office Action dated February 26, 2003, please enter the following amendment to the application, and consider the accompanying remarks.

Please cancel claims 16 and 17, without prejudice.

Please amend the claims, as follows:

1. (twice amended) A diffusion barrier coating, comprising:

(a) about 15 atom % to about 95 atom % chromium; and

(b) about 15 atom % to about 60 atom % rhenium.

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5. (twice amended) The diffusion barrier coating of claim 48, wherein the level of tungsten is in the range of about 10 atom % to about 20 atom %.

6. (amended) The diffusion barrier coating of claim 5, wherein the level of tungsten is in the range of about 10 atom % to about 15 atom %, and the level of chromium is in the range of about 15 atom % to about 90 atom %.

48. (amended) A diffusion barrier coating, comprising:

(a) about 15 atom % to about 95 atom % chromium;

and

(b) about 10 atom % to about 60 atom % tungsten.

49. (amended) A barrier coating material, comprising:

(a) about 15 atom % to about 95 atom % chromium;

(b) about 10 atom % to about 60 atom % ruthenium;

and

(c) about 1 atom % to about 15 atom % aluminum;

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

50. (amended) A diffusion barrier coating, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

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and

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

51. (amended) A diffusion barrier coating, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

(b) at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

the level of ruthenium is from about 5 atom % to about 60 atom %; and

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof,

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

52. (amended) A barrier coating material, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

(b) at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

the level of ruthenium is from about 5 atom % to about 60 atom %;

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(d) about 0.1 atom % to about 5 atom % of at least one element selected from the group consisting of zirconium, titanium, hafnium, silicon, boron, carbon, tantalum, molybdenum, and yttrium,

wherein, for the maximum level of chromium present, the sum of (a), (b), (c), and (d) is no greater than 100%.

Please add the following new claims:

New Claim 53. The barrier coating material of claim 3, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

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New Claim 54. The barrier coating material of claim 3, further comprising at least one element selected from the group consisting of tungsten, ruthenium, and mixtures of tungsten and ruthenium.

New Claim 55. The barrier coating material of claim 9, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

New Claim 56. The barrier coating material of claim 9, further comprising at least one element selected from the group consisting of rhenium, ruthenium, and mixtures of rhenium and ruthenium.

New Claim 57. The barrier coating material of claim 13, further comprising at least one element selected from the group consisting of tungsten, rhenium, and mixtures of tungsten and rhenium.

REMARKS

Restriction Requirement

Applicant has reviewed the Examiner's recent response to the previous traversal of the restriction requirement. There is still some question as to the rationale regarding the restriction, and Applicant continues to maintain that all of the claims are part of one inventive concept. However, a review of the substantive issues now takes priority over the restriction issue. Applicant does appreciate the Examiner's offer to revisit the restriction issue upon allowance of other claims in this case.

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Claim Objections

Applicant has reviewed the objection regarding claim 17, and is in agreement with the Examiner. The claim has been canceled.

Claim Rejections - 35 U.S.C. 112

Applicant has also reviewed the rejection of claims 16, 17 and 52 under this section, and is again in agreement with the Examiner. In response, claim 16 (like claim 17) has been canceled. Claim 52 has been amended, in part, to remove the inadvertent recitation of ruthenium from component (d), since the element had already been recited as part of component (b). The undersigned appreciates the Examiner pointing out these inconsistencies, since the "sorting out" of multi-element claims like these during amendments can become a bit confusing.

Claim Rejections - 35 USC 102

Claims 1, 2, 4, 10, 11, 18, 19, 48, 50 and 51 have been rejected under U.S.C. 102(b). The reference applied in the rejection is Schutz et al ("Schutz"), U.S. Patent 4,915,733. It is the Examiner's opinion that Schutz teaches metal composite powders having compositions which generally fall within the scope of the rejected claims.

Schutz describes metal composite powders, along with a process for their preparation. The powders include more than 70% by weight of at least one of molybdenum, rhenium, and tungsten. One or more binder metals are also included, such as iron, cobalt, nickel, chromium, and rhenium (col. 1, lines 57-68). The metal powders of Schutz are actually in the form of powder agglomerates, having an oxygen content of less than 1.5%. Some of the compositions noted by the Examiner appear to fall within the ranges of the pending claims.

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However, Schutz fails to disclose a "barrier coating", as in the present invention. Instead, the patent is restricted to powders. In particular, the patent is directed to "agglomerates of individual particles" (col. 1, as noted above; claim 1). Applicant submits that these particles do not anticipate the coating layer of the present invention.

In order to elucidate the concept of "coating layer", claims 1, 48, and 50-51 have been amended. The term "material" has been deleted and "diffusion" added, so that emphasis is now placed on a "diffusion barrier coating". Nothing in Schutz describes or even suggests a coating of any type. Instead, the reference appears to describe materials that are employed only in powder-related applications. Applicant thus requests that the rejections of the amended claims, as well as claims dependent therefrom, be removed.

Claim 50 has also been rejected under U.S.C. 102(b), based on a patent issued to Fischbein et al ("Fischbein"), U.S. 3,829,969. Fischbein describes protective metal layers made from certain alloy compositions. One component in the alloy is a metal such as iridium, platinum, palladium, rhenium, and the like. A second component is a metal such as chromium, manganese, niobium, tungsten, and vanadium. As the Examiner notes, a composition listed in the table of columns 9-10 contains 71 atom % chromium and 29 atom % ruthenium.

However, Fischbein fails to disclose a "barrier coating". The patent also never describes the use of a diffusion barrier layer between a substrate and an overlying layer, as in the present invention. Instead, the invention of Fischbein appears to be restricted to coatings which exhibit wear resistance and corrosion resistance (col. 2, lines 12-14). The alloy structures of the patent are designed to be sharpened and used as razor blades (e.g., col. 7, lines 28-32). These objectives have nothing to do with those of the present

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invention. As noted above, claim 50 has been amended to recite the presence of a diffusion barrier coating, and should fall outside the scope of Fischbein.

Applicant also emphasizes that the Fischbein patent is describing what appears to be an exceptionally thin coating. The patent (col. 3, lines 16-21) restricts thickness to 600 angstroms, while many of the examples (e.g., the table across columns 9 and 10) show samples with thicknesses in the range of 200 angstroms to 350 angstroms. This thickness is understandable, in view of the fact that the patent is directed specifically to very fine cutting edges for shaving instruments - not to any type of barrier structure.

Claims 5, 48, and 50-52 have been rejected under 35 U.S.C. 102(b), as being anticipated by Czech et al, U.S. Patent 5,273,712 ("Czech '712"). This patent was discussed at length in the previous Response, and describes a protective coating which contains rhenium, chromium, and optionally, other metals such as nickel, cobalt, and tungsten (col. 1, line 59-col. 2, line 19).

Czech '712 describes relatively low levels of tungsten. Czech '712 also fails to disclose a composition in the form of a barrier layer, as in the present invention. The patent is directed to specific compositions which provide corrosion and oxidation properties (col. 1, lines 54-58; col. 2, lines 19-24).

Applicant maintains that Czech '712 does not disclose the invention of claim 5. However, to reduce issues in this prosecution, the claim has been amended. The claim now recites the presence of a barrier layer, and a lower level for tungsten (about 10 atom %) in that layer. Support for the level of tungsten can be found, for example, in claim 6, as originally filed.

Claims 48, 51 and 52 have also been amended, and some of those changes are related to Czech '712. In claims 48 and 51, the tungsten

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level has also been increased to about 10%, although Applicant again emphasizes that the "diffusion barrier coating" distinguishes over this patent, even without the compositional change. Moreover, the level of rhenium in claims 51 and 52 has been increased slightly, to further distinguish over Czech '712. The change is based on the description in paragraph 19 of the specification.

Claim 50 has also been amended to emphasize the presence of a diffusion barrier layer. However, the claim is not anticipated by Czech '712 for another important reason. The claim recites a composition which "consists essentially" of chromium and at least one of rhenium, tungsten, and ruthenium. In contrast, Czech '712 requires the presence of at least one of nickel, iron, and cobalt in its coating. (See, e.g., column 1, line 63 to column 2, line 3). The presence of these elements is readily understood, since Czech '712 is directed to conventional protective coatings, as described above. The Examiner characterizes the inclusion of a metal like nickel as being merely a binder, and not altering the general composition.

Applicant must emphatically disagree, based in part on discussions with the inventors. In some instances, the presence of nickel can significantly affect the microstructural stability and melting temperature of the barrier coating of claim 50. In certain environments in which the substrate is exposed to high temperatures for long periods of time, the presence of nickel may promote greater diffusion across the barrier layer. <u>This is not to say that nickel is not a desired element in other embodiments</u>. In the present embodiment, however, nickel is excluded by the transitional phrase, and this claim cannot be anticipated by Czech '712.

Claims 21-26, 28-29, 37 and 39 are rejected under U.S.C. 102(b), as being anticipated by Jackson, U.S. Patent 4,980,244. Jackson has been discussed in earlier prosecution, in regard to other claims. In brief, the patent describes a composition consisting essentially of chromium, ruthenium,

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and aluminum. The components are present in proportions set forth within the bounds of curve A, as shown in the triaxial plot of FIG. 5 (see claim 1; and col. 2, lines 60-64).

Certainly, Jackson includes some features which are similar to those of the present invention. For example, the patent describes the use of protective coatings for turbine engine components. As discussed in the first Response, Jackson also describes some ruthenium-containing compositions which overlap some of the compositions of the present invention.

However, Jackson fails to describe the structure of claim 21. While the patent describes the presence of a metal-based substrate, it fails to describe the presence of a diffusion barrier layer between the substrate and an overlying, oxidation-resistant coating. Instead, the ruthenium-containing layer of Jackson represents <u>the protective coating itself</u> - not a barrier layer between a metal substrate and another protective layer, as in the present invention.

Moreover, Jackson fails to describe the presence of a diffusion barrier layer on a superalloy substrate, as recited in claim 26. Instead, the patent is specifically directed to higher temperature substrates, e.g., refractory substrates. (See column 1, lines 46-58; column 2, lines 15-29; and column 4, lines 19-34).

Applicant also submits that claims 28 and 29 are not anticipated by Jackson. The Examiner's statement regarding the patent's disclosure of an aluminum-rich coating over a diffusion barrier layer is not completely understood. Clarification is respectfully requested. Moreover, Applicant fails to recognize a section of Jackson which relates to aluminide or overlay coatings deposited over the diffusion barrier layer.

Furthermore, the structure recited in pending claim 37 does not appear to be found in the Jackson patent. The Examiner refers to the

discussion of an aluminum oxide layer in the patent (col. 8). However, that layer appears to be formed over what the Examiner would refer to as the "protective coating" (see line 3, page 5 of the current Office Action). Under that assumption, Jackson appears to be "missing" one layer of the claim, which recites 4 elements, in sequence: substrate, diffusion barrier layer, oxidation-resistant coating, and ceramic coating. Thus, Applicant requests that the anticipation rejection be withdrawn.

Claims 48, 50 and 51 have been rejected under 35 U.S.C. 102(b), as being anticipated by Kapoor (SIR H1146). Kapoor describes tungsten-based heavy alloys. The alloys include about 80-100 wt. % tungsten and 0-20 wt. % of at least one alloying element like molybdenum, hafnium, rhenium, chromium, and the like (col. 2, lines 15-23). Such an alloy can be further blended with copper, iron, nickel, cobalt, or tantalum (claim 3). The Examiner is correct in that there is some overlap with the presently-claimed invention, e.g., at 53 atom % tungsten and 46 atom % chromium.

However, similarity to the present invention ends at that point. Kapoor has nothing to do with alloy coatings or barrier layers. Instead, Kapoor is directed to processes (e.g., plasma rapid solidification) for making powders into spherical objects (col. 1, lines 12-15 and 61-65). These objects are presumably in the form of projectiles of some sort, e.g., kinetic energy penetration projectiles (col. 3, lines 5-12).

Claims 48, 50 and 51 include changes made herein, which serve to definitively place their subject matter outside the boundaries of Kapoor. In each claim, "barrier coating material" has been changed to "diffusion barrier coating". Since Kapoor never describes or even suggests a barrier coating, this reference should no longer be deemed to anticipate these claims.

Claim 49 has been rejected under 35 U.S.C. 102(b), as being anticipated by Prasad, U.S. Patent 4,459,263. Prasad describes a dental alloy,

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containing, primarily, cobalt, chromium, ruthenium, and aluminum. As described in the paragraph bridging columns 6 and 7, the compositions generally can include, in weight percent: 40-60% cobalt, 20-30% chromium, 5-15% ruthenium, and 1-4% aluminum. According to the Examiner, this range overlaps with that of claim 49. An example is provided in the Office Action, in which a composition is converted to the following atomic percentages: 49.7 atom % cobalt, 8.5 atom % aluminum, 8.5 atom % ruthenium, and 33.1 atom % chromium.

Prasad has little to do with the present invention. The patent is restricted to dental alloys suitable for porcelain-fused-to metal repairs (col. 1, lines 7-13; claim 1). Moreover, the compositions of Prasad specifically exclude the presence of nickel, as described in the paragraph bridging columns 1 and 2. In contrast, the open-ended language of pending claim 49 allows for nickel, which is a desirable component in some embodiments of this invention. Prasad has nothing to do with a diffusion barrier coating.

While the differences between claim 49 and Prasad appear to be evident, a small amendment has been made to reduce the issues in prosecution. Thus, the lower level of ruthenium has been changed from 5 atom % to 10 atom %. Support for the new limitation in the claim can be found in various sections of the specification, e.g., page 6, paragraph 20. As the Examiner can recognize, the highest level of ruthenium described in Prasad is 8.5 atom %. Applicant thus maintains that claim 49 is now patentable.

<u>Claim Rejections - 35 USC 103</u>

Claims 35 and 36 have been rejected under 35 U.S.C. 103(a), as being unpatentable over the Jackson reference, U.S. Patent 4,980,244. Jackson has been discussed above, and in previous prosecution. These claims relate to the thickness of the barrier layer of claim 21. It appears to be the Examiner's position that selection of a particular thickness for protection

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against environmental attack would be obvious, absent a showing of unexpected results.

Certainly, claims 35-36 are directed to barrier layer thickness. However, the claims must be interpreted in light of the claims from which they depend, e.g., claim 21 for the present invention. As noted above, Jackson fails to describe or suggest the structure of that claim.

Jackson has nothing to do with the design of a barrier layer which prevents diffusion of aluminum from an overlayer into the substrate. Instead, the patent is directed specifically to an <u>overlayer itself</u>, i.e., a protective coating for refractory-type substrates used in very high temperature applications. While Jackson does allude to the possibility of a barrier coating (col. 4, lines 51-55), there is no suggestion as to its composition.

Thus, Applicant submits that Jackson differs greatly from the present invention, <u>in addition to</u> the admitted absence of coating thickness. Without any suggestion of the foundational structure of claim 21, it would appear that no one would read the Jackson patent and envision the barrier layer thickness ranges for such a structure. It is therefore requested that the rejection of these claims be withdrawn.

Claim 38 has been rejected under 35 U.S.C. 103(a), as being unpatentable over the Jackson patent, in view of Cybulsky et al, U.S. Patent 6,168,875 ("Cybulsky"). Cybulsky describes a coating system for blade and vane components, which includes an iridium-niobium (Ir-Nb) bond coat. The bond coat is used to firmly bond an overlying thermal barrier coating (TBC) to the substrate or other underlying layers. The TBC can be a conventional, stabilized-zirconium type (claim 3). It is the Examiner's position that applying the zirconia-type TBC of Cybulsky to the turbine component described in Jackson would have been obvious, in view of the desire to protect the component from harsh environments.

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Applicant certainly agrees that Cybulsky describes the use of a conventional TBC. However, the patent is missing critical features of the present invention. For example, Cybulsky fails to suggest the use of a diffusion barrier layer similar in any way to the present invention. Instead, the patent is directed to coating structures which appear to include the Ir-Nb bond coat under the TBC but <u>over</u> a NiCoCrAlY-type protective coating. Such a layer would probably provide relatively poor oxidation resistance for the present invention. Moreover, while diffusion barrier layer 16 (FIG. 1) does lie between the protective coating 18 and the substrate 12, the barrier is based on tantalum, tantalum-nickel, or rhenium (Col. 1, lines 54-59).

Applicant does not dispute the fact that the zirconia-based TBC's described in Cybulsky are conventional. However, Cybulsky fails to "supply" the other critical features of the present invention which are missing from the Jackson patent, i.e., the specific type of barrier coating recited in claim 21. Without any suggestion of such a barrier coating, claim 38 appears to be nonobvious in view of these two references.

Claims 21-28, 35-37 and 39 have been rejected under 35 U.S.C. 103(a), as being unpatentable over Czech et al, U.S. Patent 5,273,712 ("Czech '712"), in view of Cybulsky et al. Both of these patents have been described in some detail previously. The Examiner contends that it would have been obvious to apply the zirconia thermal barrier layer of Cybulsky to the turbine component of Czech '712, to provide additional environmental protection.

Some of the compositional differences between Czech '712 and the present invention have been noted previously, in regard to other claims being examined. However, another important consideration is that Czech '712 fails to describe or suggest the presence of a <u>barrier layer</u>, i.e., a barrier layer which prevents aluminum migration from an overlying coating into an underlying substrate (e.g., see page 4, paragraph 12 of the present

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specification). Instead, Czech '712 is simply describing a typical MCrAlY-type coating which also includes rhenium (col. 1, line 59 to col. 2 line 3; col. 2, lines 19-26).

A further review of the Czech '712 patent reveals conventional objectives, such as corrosion- and oxidation-resistance at elevated temperatures. However, the patent is silent as to the objectives of the present invention, e.g., prevention of aluminum migration into the substrate, and prevention of substrate element migration into a protective coating. (See paragraph 13 of the specification). The absence of these teachings is understandable, since Czech '712 shows no recognition of the problems which prompted the present invention. Instead, the patent appears to be primarily directed to using rhenium as an economic alternative to platinum group elements in extending the service life of turbine components (col. 2, lines 19-26).

Applicant agrees with the Examiner that Czech '712 fails to describe the ceramic topcoat ("further overcoat") employed in some embodiments of the present invention. However, it is readily evident that the reference fails to even suggest the basic structure of claim 21. The second applied reference, Cybulsky, certainly provides the description of the topcoat (e.g., a TBC), but also fails to describe a coating structure similar to that of claim 21. Thus, Applicant questions the "combinability" of these two references in a way which makes the relevant claims obvious.

For these same reasons, the modified barrier layer recited in claims 24 and 25 (e.g., with additions of nickel/cobalt/iron or aluminum) appears to be nonobvious, in view of the coating structure in which the barrier layer is incorporated. Furthermore, the substrate embodiments covered in claims 26-27, protected by a coating system as recited in claim 21, are also never suggested by Czech '712 or Cybulsky. Moreover, the use of an aluminum-rich coating over the claimed barrier layer (claim 28), which

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demonstrates the utility of the barrier in preventing aluminum migration, is neither suggested nor disclosed by the references.

The Examiner refers to the coating thicknesses for the barrier layer, recited in claims 35-36. The referenced case law regarding the obviousness of the thickness of an object may be correct, in the abstract. However, such a pronouncement in no way detracts from the patentability of these particular claims. If the two cited references fail to suggest a barrier layer in a coating structure like that of claim 21, they cannot be used to make the thickness of such a layer obvious. Applicant thus requests reconsideration of this rejection.

Claims 21-27 and 39 have been rejected under 35 U.S.C. 103(a), as being unpatentable over Czech et al, U.S. Patent 5,154,885 ("Czech '885"), in view of Leverant et al, U.S. Patent 6,143,141 ("Leverant"). The Examiner contends that Czech '885 teaches a corrosion-resistant protective coating, presumably similar to the present invention, but does not describe an additional layer of metallic material, or a ceramic thermal barrier. Leverant is then described as including the additional metal (aluminide) layer. The Examiner then appears to conclude that it would have been obvious to apply Leverant's aluminide layer to a turbine component. (This is Applicant's interpretation of the last sentence of the first full paragraph on page 7 of the Office Action, but the Examiner may want to clarify the sentence).

Czech '885 describes a protective coating for metal components. The coating primarily contains rhenium and chromium. It can optionally contain aluminum, rare earth elements, and small amounts of other elements like hafnium, tungsten, and manganese. The coating is applied to nickel- or cobalt-based superalloys (col. 1, line 52 to col. 2, line 11).

However, Czech '885 fails to describe the key features of claim 21, e.g., a diffusion barrier layer between the substrate and an oxidation-

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resistant coating. Czech '885 is merely concerned with the oxidation-resistant coating itself, and improving the performance of such coatings. Czech '885 has nothing to do with the concept of preventing aluminum migration, as covered in pending claims 28-31, or the use of a barrier layer to accomplish that goal.

It appears that the Examiner is equating the conventional, oxidation-resistant coating of Czech '885 with Applicant's clamed barrier layer. This is a difficult comparison, since the barrier layer requires, for utility, a separate oxidation-resistant coating over it. Even if the layers could be equated, Czech '885's layer is quite different from Applicant's barrier material. While there may be a small amount of overlap in the comparative compositions, it can be seen that 1-20 weight percent rhenium is a much lower level than in many of Applicant's preferred embodiments. The fact that Czech '885's coating can conceivably contain only 1 weight percent rhenium is a good demonstration that the patent never contemplated the layer to be used as a barrier, as in the present invention.

Leverant describes a method of forming a diffusion barrier layer for overlay coatings. The method involves forming a first film of rhenium atoms on the surface of a superalloy substrate (col. 2, lines 19-35). The first film is then treated, e.g., with heat, to diffuse some of the rhenium into the substrate surface (col. 3, lines 16-37). Nickel-rhenium alloys are the preferred materials for the barrier layer. An overlay coating (like MCrAlY) can then be applied over the barrier layer (col. 5, lines 1-7).

Leverant fails to suggest the chromium-rhenium barrier layer materials of the present invention. Moreover, it appears that Leverant is describing a very thin layer of rhenium (e.g., submicron) as the barrier layer. Such a layer may sometimes be useful. However, as the temperature increases, e.g., to turbine engine firing temperatures, the interdiffusion between the overlayer and the substrate may become more severe. In that instance, a very

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thin layer of rhenium may be insufficient for reducing interdiffusion. (This interdiffusion can lead to reduced coating life as aluminum leaves the outer regions of the protective coating, as described in paragraphs 5-7 of the present specification).

One might then propose that thicker layers of rhenium be used in the barrier layer. However, relatively thick rhenium layers can result in a substantial mismatch in the coefficient of thermal expansion (CTE) between the barrier and the substrate. This CTE difference can cause the overlying layer to spall during thermal cycling. It was, in part, this situation which prompted conception of the particular barrier layer composition of the present invention.

Leverant never shows any recognition of these problems with rhenium-dominant barrier layers, nor does the patent suggest any solution to these problems. As shown above, Czech '885 also fails to suggest such problems, and does not even hint at the notion of using a barrier layer. For these reasons, it seems apparent that the combination of Leverant and Czech '885 cannot be made in this instance. In regard to the Examiner's conclusion, Applicant must emphasize that much more than an "aluminide layer" is missing from Czech '885, while Leverant is missing any suggestion of the particular barrier coating composition of this invention. Clearly, the two patents have the same, broad, overall objective of the present inventors: protection of metal components from a harsh, high-temperature environment. However, the means to accomplish that objective is very different.

Claims 38 and 40 have been rejected under 35 U.S.C. 103(a), as being unpatentable over Czech et al("Czech '885"), Leverant, and Cybulsky (also discussed above). These claims are directed to the presence of a top layer, i.e., a zirconia-based TBC, over the coating structure described previously, which is itself disposed on a metal substrate. It appears that the additional patent, Cybulsky, is being used to show that it would be obvious to

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apply the TBC's of Cybulsky over the structure which would result from the combined teachings of Czech '885 and Leverant.

Again, Applicant agrees that the use of TBC's over many of these protective coating systems is generally known in the art. However, Cybulsky adds nothing else to the rejection, since it is directed to something entirely different: iridium-niobium bond coats under a TBC and over a conventional, MCrAlY-type coating. As described above, the "core" of the invention is not suggested by any attempted combination of Czech '885 and Leverant, and Cybulsky adds nothing to that core, other than the TBC. Claim 38 depends on that core recitation of claim 21, while claim 40 is analogous to claim 21, albeit a bit more detailed, and supplemented by the TBC. Applicant thus requests that the Examiner reconsider this rejection.

Allowable Subject Matter

Applicant acknowledges the allowable subject matter noted on page 8 of the Office Action. It is also believed that independent claims like claim 1 and claim 48 will ultimately be allowed. Therefore, the allowable, dependent claims have not been rewritten at this time.

Several other minor changes have been made to the claims, for the sake of consistency. For example, the chromium level in claim 6 has been reduced to 90 atom %, which allows for the minimum level of tungsten in that instance, i.e., 10 atom %. (In other embodiments, the chromium level remains at 95 atom %). No new matter has been added.

A number of dependent claims have been added, and they are directed to some of the specific embodiments of the present invention. Claims 53-57 are directed to various additional components to claims 3, 9 and 13. In general, the additional components are selected from the elements nickel, cobalt or iron, and/or the elements tungsten, rhenium, or ruthenium, as set

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forth in specific claims. None of the additional claims involve new matter, as the sets of elements were recited in the original claims, and described in various sections of the specification. Since these new claims are dependent on allowable subject matter, they too should be entered here and designated as allowable.

Note Regarding Examiner's "Response to Arguments"

Applicant acknowledges the acceptance of the Rule 131 affidavit, which was directed to the Spitsberg '524 reference in the first Office Action. However, Applicant continues to maintain that the claims at issue in the relevant rejections were in fact patentable over that cited reference, absent the affidavit. Nevertheless, the affidavit did serve to advance prosecution.

Applicant also reviewed the comments made by the Examiner on page 8 of the current Office Action. The comments related to conversions between weight percent and atomic percent. The Examiner notes that the conversions do not take into consideration other elements that may be present in the barrier layer. Moreover, the Examiner maintains that the conversions show overlap with the ranges in Applicant's claims.

Applicant appreciates the Examiner's thoughts on this topic, but is unsure as to some of the points being made. While it may be true that the conversions do not always account for other materials that may be present, they do provide a benchmark for distinguishing over the cited art. As a general example, if a claim under examination requires a minimum level of 10 atom % tungsten in a given embodiment, a reference which includes a maximum tungsten level of about 5 atom % cannot anticipate the claim. This holds true, regardless of any other components that are found in the reference, and regardless of the ranges for those components. The undersigned would be happy to further discuss this issue with the Examiner.

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Applicant submits that the pending claims are now all in allowable form, as are the new claims. After the Examiner has reviewed this Response, an interview may be very helpful in resolving any remaining issues.

Respectfully submitted,

Signed by Francis T. Coppa

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5/25/03
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"Marked-up" Version of Amended Claims,
Pursuant to 37 CFR 1.121c(1)(ii)

1. (twice amended) A diffusion barrier coating [material], comprising:

(a) about 15 atom % to about 95 atom % chromium;

and

(b) about 15 atom % to about 60 atom % rhenium.

5. (twice amended) The diffusion barrier coating [material] of claim 48, wherein the level of tungsten is in the range of about [5] 10 atom % to about 20 atom %.

6. (amended) The diffusion barrier coating [material] of claim 5, wherein the level of tungsten is in the range of about 10 atom % to about 15 atom %, and the level of chromium is in the range of about 15 atom % to about 90 atom %.

48. (amended) A diffusion barrier coating [material], comprising:

(a) about 15 atom % to about 95 atom % chromium;

and

(b) about [5] 10 atom % to about 60 atom % tungsten.

49. (amended) A barrier coating material, comprising:

(a) about 15 atom % to about 95 atom % chromium;

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(b) about [5] 10 atom % to about 60 atom % ruthenium; and

(c) about 1 atom % to about 15 atom % aluminum;

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

50. (amended) A diffusion barrier coating [material], consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

and

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

51. (amended) A diffusion barrier coating [material], consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

(b) [about 5 atom % to about 60 atom % of] at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

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the level of ruthenium is from about 5 atom % to about 60 atom %; and

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof,

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

52. (amended) A barrier coating material, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

(b) [about 5 atom % to about 60 atom % of] at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

the level of ruthenium is from about 5 atom % to about 60 atom %;

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

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(d) about 0.1 atom % to about 5 atom % of at least one element selected from the group consisting of zirconium, titanium, hafnium, silicon, boron, carbon, tantalum, [ruthenium,] molybdenum, and yttrium,

wherein, for the maximum level of chromium present, the sum of (a), (b), (c), and (d) is no greater than 100%.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	
J. C. Zhao et al	:	Group Art Unit: 1775
Application No. 06/681,821	:	Examiner: J. McNeil
Filed: June 11, 2001	:	Response to Paper No. 9

For Diffusion Barrier Coatings, and Related Articles and Processes

AMENDMENT UNDER 37 CFR 1.116

Honorable Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

In response to the Office Action dated September 24, 2003, please enter the following amendment to the application, and consider the accompanying remarks.

****

CERTIFICATE OF MAILING/TRANSMISSION (37 C.F.R. 1.8(a))

I hereby certify that this paper (along with any paper referred to as being attached or enclosed) is being transmitted by facsimile to the United States Patent and Trademark Office on the date shown below.

Name of person signing certification: Francis T. Coppa

Signature: F. T. Coppa

Date: November 23, 2003

AMENDMENTS TO THE CLAIMS

Claim 1. (Currently amended) A diffusion barrier coating, comprising:

(a) about 15 atom % to about ~~95 atom %~~ 85 atom % chromium; and

(b) about 15 atom % to about 60 atom % rhenium.

Claim 2. (Original) The barrier coating material of claim 1, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

Claim 3. (Original) The barrier coating material of claim 1, further comprising about 1 atom % to about 35 atom % aluminum.

Claim 4. (Original) The barrier coating material of claim 1, wherein the level of chromium is in the range of about 25 atom % to about 60 atom %.

Claim 5. (Previously amended) The diffusion barrier coating of claim 48, wherein the level of tungsten is in the range of about 10 atom % to about 20 atom %.

Claim 6. (Currently amended) The diffusion barrier coating of claim 5, wherein the level of tungsten is in the range of about 10 atom % to about 15 atom %~~, and the level of chromium is in the range of about 15 atom % to about 90 atom %~~.

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Claim 7. (Original) The barrier coating of claim 5, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

Claim 8. (Original) The barrier coating material of claim 5, further comprising about 5 atom % to about 30 atom % of nickel.

Claim 9. (Original) The barrier coating material of claim 5, further comprising about 1 atom % to about 35 atom % aluminum.

Claim 10. (Original) The barrier coating material of claim 1, wherein the level of rhenium is in the range of about 15 atom % to about 35 atom %.

Claim 11. (Original) The barrier coating of claim 10, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

Claim 12. (Original) The barrier coating material of claim 10, further comprising about 1 atom % to about 35 atom % aluminum.

Claim 13. (Canceled)

Claim 14. (Currently amended) The barrier coating material of ~~claim 13~~ claim 49, wherein the level of ruthenium is in the range of about 20 atom % to about 40 atom %.

Claim 15. (Currently amended) The barrier coating material of ~~claim 13~~ claim 49, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

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Claims 16-17. (Canceled)

Claim 18. (Original) The barrier coating material of claim 1, wherein the level of rhenium is in the range of about 40 atom % to about 60 atom %.

Claim 19. (Original) The barrier coating material of claim 18, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

Claim 20. (Original) The barrier coating material of claim 18, further comprising about 1 atom % to about 35 atom % aluminum.

Claim 21. (Original) An article for use in a high-temperature, oxidative environment, comprising:

(i) a metal-based substrate, comprising aluminum and other alloy elements;

(ii) a diffusion barrier layer overlying the substrate, said layer comprising

(A) about 15 atom % to about 95 atom % chromium; and

(B) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; and

(iii) an oxidation-resistant coating over the diffusion barrier layer.

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Claim 22. (Original) The article of claim 21, wherein the level of chromium in the diffusion barrier layer is in the range of about 50 atom % to about 95 atom %.

Claim 23. (Original) The article of claim 21, wherein the level of chromium is in the range of about 25 atom % to about 60 atom %.

Claim 24. (Original) The article of claim 21, wherein the diffusion barrier layer further comprises about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

Claim 25. (Original) The article of claim 21, wherein the diffusion barrier layer further comprises about 1 atom % to about 35 atom % aluminum.

Claim 26. (Original) The article of claim 21, wherein the metal-based substrate is a superalloy, and comprises at least one base metal selected from the group consisting of nickel, cobalt, and iron.

Claim 27. (Currently amended) The article of claim 26, wherein the substrate further comprises at least one alloy element selected from the group consisting of ~~cobalt~~, aluminum, chromium, hafnium, yttrium, molybdenum, titanium, tantalum, carbon, and boron.

Claim 28. (Original) The article of claim 21, wherein the oxidation-resistant coating of component (iii) is an aluminum-rich coating, and the diffusion barrier layer of component (ii) prevents the substantial migration of aluminum from the aluminum-rich coating to the substrate, while also preventing the substantial migration of alloy elements of the substrate into the aluminum-rich coating.

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Claim 29. (Original) The article of claim 28, wherein the aluminum-rich coating over the diffusion-barrier layer is an aluminide coating or an overlay coating.

Claim 30. (Original) The article of claim 29, wherein the aluminide coating is selected from the group consisting of nickel-aluminide; noble metal-aluminide, and nickel-noble metal-aluminide.

Claim 31. (Original) The article of claim 30, wherein the noble metal is platinum.

Claim 32. (Original) The article of claim 21, wherein the oxidation-resistant coating of component (iii) is an overlay coating having the composition MCrAl(X), where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof.

Claim 33. (Currently Amended) The article of claim 21, wherein the oxidation-resistant coating of component (iii) comprises a ~~nickel-chrome~~ nickel-chromium alloy.

Claim 34. (Currently Amended) The article of claim 33, wherein the ~~nickel-chrome~~ nickel-chromium alloy contains about 20 atom % to about 50 atom % chromium, and further comprises at least one element selected from the group consisting of manganese, silicon, and a rare earth element.

Claim 35. (Original) The article of claim 21, wherein the barrier layer has an average thickness in the range of about 1 micron to about 50 microns.

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Claim 36. (Original) The article of claim 35, wherein the barrier layer has an average thickness in the range of about 5 microns to about 20 microns.

Claim 37. (Original) The article of claim 21, further comprising a ceramic coating disposed over the oxidation-resistant coating of component (iii).

Claim 38. (Original) The article of claim 37, wherein the ceramic coating is a zirconia-based thermal barrier coating.

Claim 39. (Original) The article of claim 21, wherein the substrate is an airfoil of a gas turbine engine.

Claim 40. (Currently Amended) A turbine engine component for use in a high-temperature, oxidative environment, comprising:

(I) a superalloy substrate, comprising a nickel or nickel-cobalt alloy;

(II) a diffusion barrier layer overlying the substrate, said layer comprising

(a) about 15 atom % to about 95 atom % chromium;

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof;

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(c) about 1 atom % to about 35 atom % of at least one element selected from ~~at least one element selected from~~ the group consisting of nickel, cobalt, iron, and combinations thereof; and

(d) about 1 atom % to about 35 atom % aluminum,

wherein, for the maximum level of chromium present, the sum of (a), (b), (c), and (d) is no greater than 100%;

(III) an oxidation-resistant coating over the diffusion barrier layer, comprising a material selected from the group consisting of aluminide materials, MCrAl(X) materials, and ~~nickel-chrome~~ nickel-chromium materials,

where M is an element selected from the group consisting of Ni, Co, Fe, and combinations thereof; and X is an element selected from the group consisting of Y, Ta, Si, Hf, Ti, Zr, B, C, and combinations thereof; and

(IV) a zirconia-based thermal barrier coating over the oxidation-resistant coating.

Claims 41-47 (Withdrawn)

Claim 48. (Currently amended) A diffusion barrier coating, comprising:

(a) about 15 atom % to about ~~95~~ 90 atom % chromium; and

(b) about 10 atom % to about 60 atom % tungsten.

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Claim 49. (Previously amended) A barrier coating material, comprising:

(a) about 15 atom % to about 95 atom % chromium;

(b) about 10 atom % to about 60 atom % ruthenium;

and

(c) about 1 atom % to about 15 atom % aluminum;

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

Claim 50. (Currently Amended) A diffusion barrier coating, having a thickness in the range of about 1 micron to about 50 microns, and consisting essentially of:

(a) about ~~15~~ 40 atom % to about 95 atom % chromium;

and

(b) about 5 atom % to about 60 atom % of at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof.

Claim 51. (Previously amended) A diffusion barrier coating, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

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(b) at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

the level of ruthenium is from about 5 atom % to about 60 atom %; and

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof,

wherein, for the maximum level of chromium present, the sum of (a), (b), and (c) is no greater than 100%.

Claim 52. (Previously amended) A barrier coating material, consisting essentially of:

(a) about 15 atom % to about 95 atom % chromium;

(b) at least one element selected from the group consisting of rhenium, tungsten, ruthenium, and combinations thereof; wherein for each element which may be present:

the level of rhenium is from about 15 atom % to about 60 atom %;

the level of tungsten is from about 10 atom % to about 60 atom %; and

the level of ruthenium is from about 5 atom % to about 60 atom %;

(c) about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof; and

(d) about 0.1 atom % to about 5 atom % of at least one element selected from the group consisting of zirconium, titanium, hafnium, silicon, boron, carbon, tantalum, molybdenum, and yttrium,

wherein, for the maximum level of chromium present, the sum of (a), (b), (c), and (d) is no greater than 100%.

Claim 53. (Previously added) The barrier coating material of claim 3, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

Claim 54. (Previously added) The barrier coating material of claim 3, further comprising at least one element selected from the group consisting of tungsten, ruthenium, and mixtures of tungsten and ruthenium.

Claim 55. (Previously added) The barrier coating material of claim 9, further comprising about 1 atom % to about 35 atom % of at least one element selected from the group consisting of nickel, cobalt, iron, and combinations thereof.

Claim 56. (Previously added) The barrier coating material of claim 9, further comprising at least one element selected from the group consisting of rhenium, ruthenium, and mixtures of rhenium and ruthenium.

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Claim 57. (Currently amended) The barrier coating material of ~~claim 13~~ claim 49, further comprising at least one element selected from the group consisting of tungsten, rhenium, and mixtures of tungsten and rhenium.

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REMARKS

Claims 1-15, 18-40 and 48-57 are pending in the application. Claims 41-47 had been withdrawn from consideration, pursuant to a previous Restriction Requirement. At this time, all of the claims have been allowed, except for claim 50. (The last-mentioned claim is discussed below). Applicant has reviewed the other allowed claims, and made a number of changes, which are briefly discussed below.

Claim 1 has been amended to change the maximum amount of chromium from 95 atom % to 85 atom %. Applicant emphasizes that this change is not being made to avoid any prior art. Instead, the change is made to allow for a minimum amount of rhenium, i.e., 15 atom %, as recited for component (b) of the claim. This type of change has been made to other claims earlier on in prosecution, with the approval of the Examiner. No new matter is being inserted.

Claim 6 has been amended to delete the recitation of a range of chromium, since that range was redundant in view of the amendment to claim 48, discussed below.

Claim 13 has been canceled, in view of the fact that the level of ruthenium was redundant in view of previously-amended claim 49. Claims 14 and 15, which previously depended from claim 13, have been changed to depend from claim 49. (Claims 16-17 had been canceled in a previous Response).

Claim 27 has been amended in several ways. Cobalt has been removed from the claim, in view of it already being recited in claim 49. In addition, other elements which are often found in superalloy substrates have been added. Support for the additional elements can be found, for example, in

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paragraph 17 of the specification. No new matter has been added, and the claim merely represents a more specific embodiment than claim 26.

Claims 33 and 34 have been changed, so that the term "nickel-chromium" is used in place of "nickel-chrome". Arguably, the terms have the same definition, but "nickel-chromium" might sometimes be preferred. Compositions of this type are generally described in paragraph 38 of the specification. The same type of change is made in claim 40.

Additional language has been added to claim 40, specifying that the components in paragraph (II) of the claim are present in a sum no greater than 100%. Such language does not add new matter, and could in fact be inferred from the original language. The additional phrase simply allows for the minimum levels of components (b) to (d) when component (a) is present at its maximum level. (Adjustment of the maximum level of chromium would be an alternative method of making the same point. Such a change was made in claim 48, reducing the chromium level to account for the minimum level of tungsten). Lastly, a slight change was made for component (c), to improve "readability".

Claim 50 remains rejected under 35 U.S.C. 102(b), in view of Fischbein et al ("Fischbein"), U.S. 3,829,969. The reference has been discussed in detail in previous correspondence. Applicant continues to maintain that the patent fails to describe a "barrier coating", as in the present invention. Moreover, the use of such a coating between a substrate and an overlying layer is also never described. Furthermore, the coating which Fischbein does describe is extremely thin. As discussed in a previous Response, that feature seems to be in line with Fischbein's use of the coated article as a shaving instrument.

In contrast to the Examiner's position, Applicant maintains that the term "barrier" does provide a structural definition to the coating. The

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concept of a barrier in this particular application is described at length in the specification, e.g., paragraph 12. There is no evidence that the coating in Fischbein - especially at its prescribed thickness - could perform such a function.

To summarize, Applicant maintains that claim 50 is not anticipated by Fischbein. However, to reduce issues and conclude prosecution, the claim is now being amended. As set forth above, a thickness for the coating is now recited in the claim. Support for the thickness range is found in various sections of the application, e.g., paragraph 32 and claim 35. The range of about 1-50 microns is somewhat approximate. However, that range far exceeds the thickness of the coatings in Fischbein, which appear to have a maximum thickness of 600 Angstroms (column 3, lines 16-21). In view of these remarks and amendments, Applicant submits that claim 50 should now be allowed.

One other change is being made to the claim, however. The lower level of chromium in component (a) is being raised to about 40 atom %. This change is not intended to narrow the scope of the claim, but to instead account for the maximum level of elements in component (b), i.e., about 60 atom %. In this instance, the transitional term "consisting essentially of" generally excludes other materials which would materially affect the composition. (However, Applicant does wish to emphasize that other materials could be present in the composition of claim 50, as long as they do not significantly change its characteristics.)

It is Applicant's view that all of the pending claims are ready to issue, with the approval of the Examiner. Any remaining issues are hopefully minor, and capable of being handled over the telephone.

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Respectfully submitted,

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